Rhodium(I) ferrocenylcarbene complexes: Synthesis, structural determination, electrochemistry and application as hydroformylation catalyst precursors.

G. Kabelo Ramollo[a], María J. López-Gómez[a], David C. Liles[a], Leah C. Matsinha[b], Gregory S. Smith[b] and Daniela I. Bezuidenhout[a*]

[a] Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield 0028, South Africa.

[b] Department of Chemistry, University of Cape Town, Private Bag, Rondebosch 7701, South Africa.

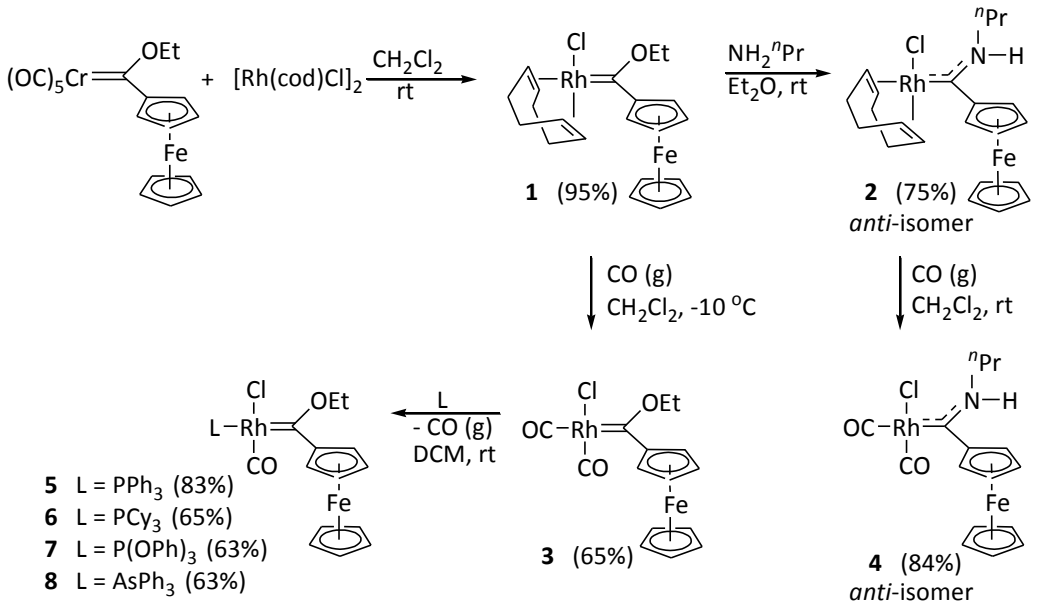
ABSTRACT: New examples of the rare class of rhodium(I) ferrocenyl Fischer carbene complexes **1–8**, [Rh(LL)Cl{C(XR)Fc}] [LL = cod, $(CO)_2$, (CO, PR_3) (R = Ph, Cy or OPh) and (CO, $AsPh_3$); XR=OEt or NH^nPr] were prepared, and the electronic effects of co-ligands and alkoxy *vs.* aminocarbene substituents were investigated by spectroscopic and electrochemical methods. The molecular structures of complexes **1**, **2** and **4–6** were confirmed by single crystal X-ray diffraction. The use of the complexes **1–8** as homogeneous catalysts for the hydroformylation of 1-octene was demonstrated, and the influence of the carbene substituents and co-ligands on the activity and regioselectivity of the catalysis evaluated. Finally, the stability of the Rh-$C_{carbene}$ bond of complex **1** under hydroformylation conditions was confirmed with ^{13}C NMR experiments.

INTRODUCTION

The importance of optimizing the ligand structure of homogeneous rhodium(I) complexes for the industrially important hydroformylation reaction is well-known, where sufficient electron density on the rhodium(I) center is required for maximum conversion of terminal olefins to the more preferred linear aldehydes as desired hydroformylation product for most applications.[1] As the catalytic mechanism for this conversion is well-understood, the modulation of the steric and electronic properties of the commonly-used phosphane ligands has been directed towards the optimization of both the activity and the selectivity of these rhodium-based catalysts. Specifically, an increase in the *n*/*iso* ratio of the aldehydes has been found due to a high steric demand around the rhodium-center when excess phosphanes were employed, or when phosphanes with stronger π-acceptor properties were used.[1]

With the advent of the versatile N-heterocyclic carbenes (NHCs), a new class of carbon-based ligands with similar binding properties as phosphanes was introduced.[2] NHCs with their strong σ-donor and poor π-accepting properties yield stable metal-NHC complexes,[3] and a number of rhodium(I)-NHC complexes has been reported for application in the hydroformylation of olefins.[4] Significant improvement in the alkene conversion, activity and selectivity to the linear aldehydes was observed when increasing the electron-withdrawing capacity of the modifying ligand. This can be achieved by the reduction of the strong electron-donor properties of NHC ligand *via* inclusion of electron-withdrawing N-substituents on the NHC, or by combination with an electron-withdrawing phosphane or phosphite as co-ligand. This conclusion prompted the investigation into the use of electrophilic Fischer carbene complexes of rhodium(I) as catalyst precursors for the hydroformylation of 1-octene.[5] Examples of isolated rhodium(I) Fischer carbene complexes are rare,[6] although they have been implicated as the catalytically active intermediates in the cyclisation of allenes[7] and alkynes[8] with Group 6 Fischer alkenylcarbene complexes.

The use of rhodium(I) Fischer carbene complexes in the catalytic hydroformylation of alkenes are unexplored in the literature. Herein we report the synthesis of a range of ferrocenyl-substituted rhodium(I) Fischer carbene complexes and the investigation of their application as



Scheme 1. Synthesis of rhodium(I) ferrocenyl Fischer carbene complexes **1–8**.

catalysts in the hydroformylation reaction of 1-octene.This constitutes one of the few examples of the catalytic use of Fischer carbene complexes.[9]Ferrocene was included as carbene substituent in an effort to stabilize the electrophilic Fischer carbene ligand, in order to prevent carbene ligand dissociation. This approach of including a second metal also confers possible advantages such as improved activity and increased reaction rates, specifically involving examples where one metal acts as the main catalytic center whereas the other metal serves as an electron reservoir.[10]

RESULTS AND DISCUSSION

Synthesis and characterization of rhodium(I) ferrocenylcarbene complexes. Until the independent reports of the catalytic transfer of a carbene ligand from a Group 6 Fischer carbene complex to a palladium reagent by Sierra and co-workers[11] and Narasaka and co-workers,[12] the use of Fischer carbene ligands to adjust the reactivity of late transition metal complexes was mostly undeveloped, and the first examples of cationic rhodium(I) Fischer carbene complexes obtained via a transmetalation reaction from the pentacarbonyl Group 6 transition metal precursor were only reported thereafter.[6b,13]

This investigation was initiated by first attempting the stoichiometric transmetalation of the chromium(0) heteroaryl ethoxycarbene complexes (heteroaryl = 2-thienyl or 2-furyl)[14] with[Rh(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene), in a modified procedure to that described by Barluenga *et al.* for the preparation of neutral rhodium(I) alkenylcarbene complexes;[6a] however only the self-dimerization products could be isolated after column chromatography. The decomposition self-dimerization products include a carbene-carbene coupled olefin as well as the regeneration of the rhodium precursor, analogously to the carbene dimerization decomposition observed for other late transition metal Fischer carbenes.[15]

Table 1. Spectroscopic data for complexes **1–8**.

Com-plex	^{13}Cδ($C_{carbene}$)[a], (^1J(RhC) and ^2J(PC) (Hz))	^{13}C δ(CO)[a], (^1J(RhC)and ^2J(PC) (Hz))	IR[b] ν(CO) (cm^{-1})	IR[b] ν_{av}(CO), TEP[e] (cm^{-1})
1	302 (d, 43)	-	-	-
2	258 (d, 40)	-	-	-
3	289 (d, 38)	187 (d, 50)[c] 183 (d, 77)[d]	2001[d] 2084[c]	2042 2054[e]
4	238 (d, 35)	187 (d, 51)[c] 184 (d, 78)[d]	1995[d] 2077[c]	2036 2049[e]
5	300 (dd, 110, 40)	188 (dd, 81, 16)[d]	1965[d]	-
6	303 (dd, 103, 39)	189 (dd, 83, 17)[d]	1946[d]	-
7	298 (dd, 174, 39)	185 (dd, 79, 21)[d]	1986[d]	-
8	295 (d, 45)	187 (d, 80)[d]	1966[d]	-

*[a]Recorded in $CDCl_3$. [b]Recorded in CH_2Cl_2. [c]CO-ligand trans to carbene. [d]CO-ligand trans to Cl. [e]Calculated using the linear regression model TEP = 0.8001ν_{av}(CO)**Rh** + 420 cm^{-1}.[3a]*

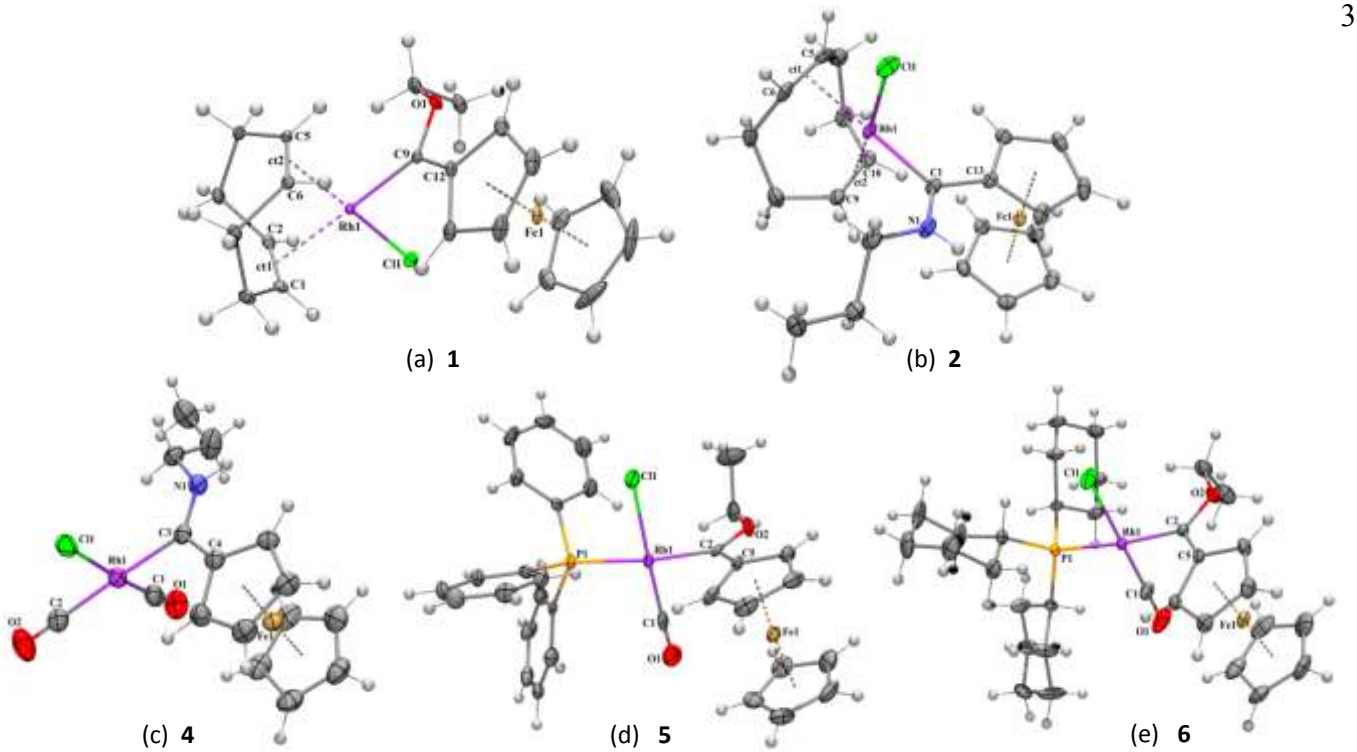


Figure 1. Molecular structures of (a) **1**, (b) **2**, (c) **4**, (d) **5** and (e) **6**, showing 50% probability ellipsoids and partial atom-numbering schemes. Two CH_2Cl_2 solvent molecules were omitted from the structure of **5** for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes **1**, **2**, **4**–**6**.

Bond lengths	**1**	**2**	**4**	**5**	**6**
Rh-$C_{carbene}$	1.958(2)	2.018(1)	2.06(1)	2.017(4)	2.027(1)
$C_{carbene}$-O/N	1.322(3)	1.308(2)	1.305(3)	1.312 (7)	1.312(2)
$C_{carbene}$-$C_{ipso\text{-}Fc}$	1.448(3)	1.467(2)	1.470(3)	1.448(6)	1.441(2)
Rh-Cl	2.375(1)	2.391(1)	2.374(1)	2.381(1)	2.374(1)
Rh-Y[a,b] or Rh-CO_{trans}	2.005(1)[a]	1.988(1)[b]	1.826(2)	1.832(6)	1.799(2)
Rh-Y[c,d] or Rh-CO_{cis}[e] or Rh-P[f]	2.166(1)[c]	2.104(1)[d]	1.932(3)[e]	2.329(1)[f]	2.357(1)[f]
Bond angles					
$C_{carbene}$-Rh-Cl	94.90(7)	87.61(4)	88.12(6)	86.4(1)	86.28(4)
O/N-$C_{carbene}$-$C_{ipso\text{-}Fc}$	109.3(2)	115.6(1)	116.1(2)	111.5(4)	110.5(1)
Torsion angles					
$C_{\alpha\text{-}Fc}$–$C_{ipso\text{-}Fc}$–$C_{carbene}$–O/N	1.8(3)	3.4(2)	11.5(3)	3.4(2)	1.9(2)

[a]*Y= midpoint of C(5)–C(6).* [b]*Y = midpoint of C(1)–C(6).*[c]*Y= midpoint of C(1)–C(2).* [d]*Y = midpoint of C(9)–C(10).*

It was reasoned that the electrophilic Fischer carbene ligand in Barluenga's system was stabilized by the stronger donating NHC co-ligand, and hence it was decided to similarly circumvent self-dimerization by modifying the Group 6 Fischer carbene precursor to contain the more donating, redox-active ferrocenyl (Fc) substituent.[16]

The precursor chromium(0) ferrocenyl ethoxycarbene complex was prepared according to literature procedures,[17] dissolved in a dichloromethane solution with an equimolar amount of rhodium precursor at room temperature, and stirred for 14 days. The desired product [Rh(cod)Cl{C(OEt)Fc}] (**1**)was isolated in high yield (95%) after column chromatography, whereafter it was employed as starting material for the preparation of complexes **2**–**8** (see Scheme 1). To compare with a more donating carbene ligand, the ethoxycarbene substituent was replaced with an *n*-propylamino-substituent by direct aminolysis of the alkoxycarbene with the primary amine in diethyl ether.[18] The availability of the nitrogen lone pair for donation towards the carbene carbon results in an

increased $C_{carbene}$–N bond order.[19] Surprisingly, both NMR and single crystal X-ray diffraction studies confirm that only the *anti*-aminocarbene isomer [Rh(cod)Cl{C(NH^{n}Pr)}] (**2**, 75 %) is obtained due to restricted rotation around the $C_{carbene}$-N bond and the steric bulk of the ferrocenyl substituent.[20]

The substitution of the cyclooctadiene ligand was also effected, in an effort to investigate the effect of other π-acceptor ligands in the metal coordination sphere with regards to the activity and selectivity of the prepared complexes as hydroformylation catalysts. To this end, carbon monoxide gas was bubbled through dichloromethane solutions of **1** and **2** at -10 °C or at room temperature, respectively. The dicarbonyl carbene complex **3**, [Rh(CO)$_2$Cl{C(OEt)Fc}] (65%) and **4**, [Rh(CO)$_2$Cl{C(NH^{n}Pr)Fc}] (84%), were isolated after recrystallization by layering the dichloromethane reaction mixture with hexanes. The *anti*-conformation around the $C_{carbene}$-N bond of the aminocarbene ligand of **4** is retained, with the H-atom on the amino moiety orientated towards the Fc-substituent (see Figure 1). Finally, one of the carbonyl ligands of **3** could be substituted by a phosphane, phosphite or arsane ligand, by reaction of one equivalent of PR_3 (R = Ph, Cy or OPh) or $AsPh_3$ in dichloromethane at room temperature to yield complexes [Rh(CO)(L)Cl{C(OEt)Fc}]**5** (L = PPh3), **6** (L = PCy3), **7** {L = P(OPh)3}and **8** (L = AsPh3) in yields ranging from 63–83%.

Compounds **1–8** were characterized by NMR and FT-IR spectroscopy and mass spectrometry, and single crystals for X-ray diffraction could be obtained for **1**, **2** and **4–6**. The spectroscopic data clearly verify the presence of the carbene and the CO ligands, with Rh-$C_{carbene}$ doublet resonances for the ethoxycarbene complexes **1**, **3** and **5–8** ranging between 289 – 303 ppm, and for the aminocarbene complexes **2** and **4** the values are 258 and 238 ppm, respectively. These values are slightly upfield from those reported by Barluenga and co-workers (307 – 314 ppm for the alkoxycarbene complexes and 243 – 245 ppm for the aminocarbene complexes)[6a] (see Table 1). Presumably the upfield shift is due to the increased donating ability of the ferrocenylcarbene ligand compared to the alkenylcarbenes. In both the ^{1}H and ^{13}C NMR spectra of compounds **1–8**, four different proton and carbon resonances, respectively, are observed for the substituted cyclopentadienyl ring of the ferrocenyl moiety. This clearly indicates the hindered rotation of the ferrocenyl groupin contrast to the symmetric substitution pattern observed (only two proton and carbon resonances, respectively) for the precursor chromium ferrocenylcarbene complex.[14,19]The carbonyl ^{13}C resonances are relatively insensitive to the changes in the electronic properties of the metal. The infrared carbonyl stretching frequencies of the monocarbonyl carbene complexes **5–8** (Table 1) give a better reflection of the donating ability of the electronic environment around the Rh(I) centre, and correlate with the expected donor ability of the ligands in the order PCy_3 > PPh_3 , $AsPh_3$ > $P(OPh)_3$.[21] In the case of the two dicarbonyl carbene complexes **3** and **4**, the ν_{av}(CO) could be used to estimate and compare the stereoelectronic properties of the ferrocenyl ethoxycarbene ligand and the ferrocenyl aminocarbene ligand with each other, and known imidazolylidene-based NHCs. This was done by calculating the TEP (Tolman electronic parameter) using the simple linear regression model reported by Glorius[3a] to correlate ν_{av}(CO) of [RhCl(carbene)(CO)$_2$] with the TEPs for the [LNi(CO)$_3$] system originally described by Tolman,[21] and expanded for [IrCl(carbene)(CO)$_2$][22] and [RhCl(carbene)(CO)$_2$].[23] The TEPs calculated for **3** (2054 cm^{-1}) and **4** (2049 cm^{-1}) demonstrate, to the best of our knowledge, for the first time the comparable donor strength of both ferrocenylcarbene ligands with known saturated and unsaturated NHCs with TEPs ranging between 2055 – 2049 cm^{-1},[22b]and also indicate the more donor character of the aminocarbene *vs* the alkoxycarbene ligands.

The molecular structures of **1**, **2**, **4–6** were confirmed by single crystal X-ray structure analyses (Figure 1), and selected bond distances and angles are presented in Table 2. The complexes display *pseudo*-square planar (**1**, **2**) or square planar geometry (**4–6**) at the rhodium(I) center, with Rh–$C_{carbene}$ bond distances ranging from 1.958(2)–2.061(2) Å. The Rh–$C_{carbene}$ bond lengths are comparable to those reported for previously isolated Rh(I) Fischer carbene complexes (1.930–2.113 Å).6 The increased Rh–Ccarbene distance of the aminocarbene complex 2 (2.0178(13) Å) compared to the ethoxy-analogue 1 (1.958(2) Å), is indicative of the greater carbene carbon stabilization from the N-heteroatom compared to the O-carbene substituent, and resultant decreased π-backbonding required from the rhodium metal towards the carbene carbon atom. Likewise, shorter $C_{carbene}$–N bond distances (1.3083(18) Å for **2**; 1.305(5) Å for **4**) compared to the $C_{carbene}$–O bond lengths (1.3116(16)–1.322(3) Å for **1**, **5** and **6**) and less acute N–$C_{carbene}$–C_{Fc} bond angles (115.56(12)° for **2**, 116.1(2)° for **4**) compared to the O–$C_{carbene}$–C_{Fc} bond angles (109.3(2)–111.5(4) Å for **1**, **5** and **6**), also attest to the increased $C_{carbene}$-N bond order. Additionally, the effect of the π-acidic carbonyl ligands in **4** (Rh–$C_{carbene}$ distance = 2.061(2) Å) on the π-back donation of the metal to the carbene carbon in **2** (Rh–$C_{carbene}$ distance = 2.0178(13) Å)

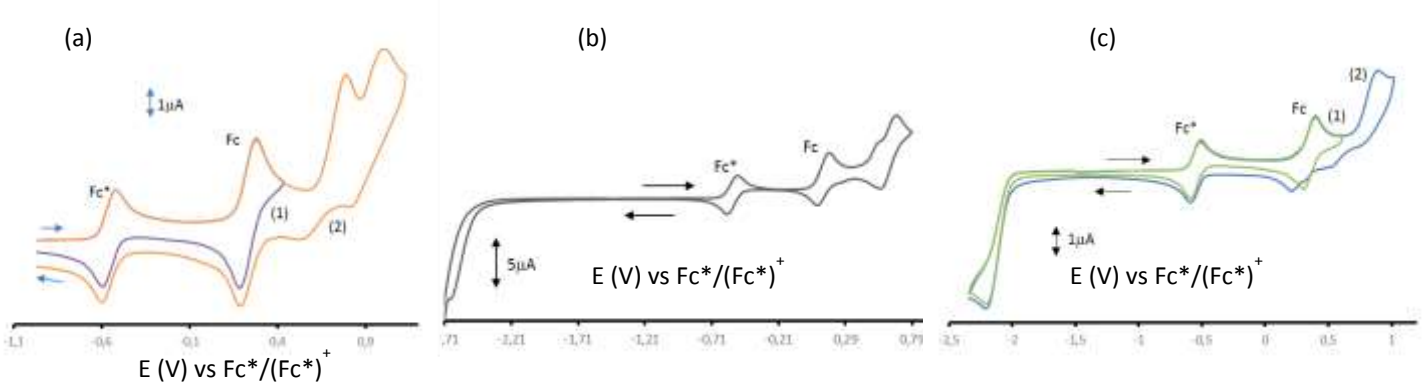


Figure 2. The cyclic voltammograms of (a) [Rh(cod)Cl{C(OEt)Fc}] (**1**), (b) [Rh(cod)Cl{C(NH^{n}Pr)Fc}] (**2**) and (c) [Rh(CO){P(OPh)$_3$}Cl{C(OEt)Fc}] (**7**) respectively, at a glassy carbon electrode, scan rate 0.1 V s^{-1} in CH_2Cl_2, with the internal standard used (marked as Fc*).

In like manner, the Rh–CO bondlengths of the carbonyl ligands *trans* to the chlorido-ligand are all significantly shorter (1.799(2) –1.832(6) Å), than that of the Rh–CO bondlength of the CO *trans* to the carbene ligand in **4** (1.932(3) Å). The steric bulk of the co-ligand *trans* to the carbene influences the rotational freedom of the ferrocenyl moiety. The $C_{\alpha\text{-}Fc}$–$C_{ipso\text{-}Fc}$–$C_{carbene}$–O/N torsion angle for the bulky cod- (**1**, 1.8(3)°; **2**, 3.4(2)°) and the phosphane-substituted complexes (**5**, 3.4(2)°; **6**, 1.9(2)°) are significantly smaller than the torsion angle of 11.5(3)° observed for the dicarbonyl complex **4** (see Table 2).

Cyclic Voltammetry. The approach to monitor changes in the carbonyl stretching frequencies of carbonyl complexes via infrared spectroscopy is the classic method to evaluate the electron donating properties of ligands. However the electrochemical approach, where the redox potentials are determined by cyclic voltammetry, is a more sensitive tool for determining the electronic environment surrounding the central rhodium(I) metal. The redox potentials of Ru(II/III) metal complexes have been used to establish the Lever electronic parameters (LEP), which reflect the donor capacity of the ligands bound to the Ru-metal.[24] Although correlations between LEPs and TEPs are rare,[25] correlations between ν(CO) in [Rh(CO)$_2$Cl(carbene)] and the Rh(I/II) redox potentials have been reported.[23]Also, the redox potentials do not directly provide information on the electron-donating capacity of a given ligand, but represent the energy difference between the reduced metal complex and the oxidized metal complex.

The cyclic voltammograms (CVs) of **1–8** at a glassy carbon electrode in CH_2Cl_2 show irreversible reduction of the carbeneat *ca.* -2.3 V, reversible oxidation of the ferrocenyl moiety at *ca.* 0.2 V and ill-defined peaks related to the Rh(I/II) and Rh(II/III) couples at higher potentials, ranging between 0.52 V for **2** and 1.02 V for **1** (*vs.* Ag/Ag$^+$, E°′= -0.54 V for the couple $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+1/0}$ as an internal standard, referenced to the ferrocene/ferrocenium couple at 0V).

Table 3. Potentials (V) for the three redox processes observed for complexes **1–8** *vs.* the Ag/Ag$^+$ couple using the redox couple $[Fe(\eta\text{-}C_5Me_5)_2]^{+1/0}$ as internal standard in the test solutions.

Complex	$E_{p,}^{red}$ (V) [Rh=C/$^-$Rh-C$^\cdot$]	E°′ (V) [Fe(II/III)]	E_p^{ox} (V) [Rh(I/II)], [Rh(II/III)]
1	-2.42	0.25	0.80, 1.02
2	-2.60	0.13	0.52, 0.69
3	-1.95	0.36	-[b]
4	-2.30	0.24	0.87[a]
5	-2.30	0.28	0.54, 0.59
6	-2.34	0.28	0.66, 0.79
7	-2.16	0.31	0.92[a]
8	-2.20	0.29	0.61, 0.71

[a]*Overlapping waves of [Rh(I/II)] and [Rh(II/III)].*[b]*Not observed in the solvent window employed.*

The values obtained for **1–8** are summarized in Table 3. The CV of **1**, from -1.05 V to 1.3 V, shows three oxidation waves with peak potentials, at E°′ = 0.25 V and, E_p^{ox} = 0.80 and 1.02 V (Figure 2a (2)). When the scan was curtailed at 0.4 V (Figure 2a(1)), the first oxidation wave was reversible. Thus, the one-electron oxidation product of **1**, [Rh(cod)Cl{C(OEt)Fc}] $^+$, is stable on the CV timescale.

Table 4. Hydroformylation of 1-octene with catalyst precursors **1–8**.Reactions[a] were carried out with ($CO:H_2$) (1:1) at 40 bar, 80 °C in toluene (5 mL) with 6.37 mmol of 1-octene and 0.0039 mmol Rh catalyst. After 4 hours, the GC conversions were obtained using *n*-decane as an internal standard in relation to authentic standard internal octenes and aldehydes.

Catalyst	% Conversion	% Total Aldehydes	% Internal Octenes	% *n*-Aldehydes	n/isoratio	TOF[b]
1	100	100	0	44 (4.0)	0.79 (0.130)	418 (14.2)
1[c]	91 (1.0)	63 (11.1)	37 (11.1)	62 (0.1)	1.63 (0.01)	256 (51.7)
1[d]	98 (0.6)	58 (7.9)	42 (7.9)	70 (2.1)	2.37 ((0.240)	233 (29.0)
1[e]	90 (10.1)	55 (4.0)	45 (4.0)	62 (8.7)	1.69 (0.610)	204 (40.0)
2	100	90 (2.3)	10 (2.3)	55 (3.0)	1.25 (0.160)	366 (9.0)
3	100	100	0	50 (1.2)	0.98 (0.047)	379 (14.1)
4	99 (0.1)	85 (0.5)	15 (0.5)	57 (3.8)	1.33 (0.210)	343 (8.3)
5	100	100	0	49 (2.7)	0.98 (0.100)	407 (0.9)
6	100	94 (1.2)	6 (1.2)	55 (1.1)	1.20 (0.050)	380 (3.9)
7	100	100	0	51 (0.5)	1.06 (0.020)	409 (27.2)
8	100	85 (2.4)	15 (2.4)	57 (2.7)	1.32 (0.140)	346 (10.0)

[a]Reactions were performed in triplicate, and the standard deviations given in brackets for all results. [b]TOF = (mol aldehydes/mol cat.)h^{-1}. [c]Reaction conditions 40 bar, 70 °C, 4hrs. [d]Reaction conditions 30 bar, 80 °C, 4 hrs. [e]Reaction conditions 20 bar, 80 °C, 4 hrs.

This result is consistent with that shown for **7** in Figure 2c. The CV of **2** from -2.71 to 0.79 V (Figure 2b) shows one reduction wave with peak potential, E_p^{red} = -2.60 V and three oxidation waves with peak potentials at E°′ = 0.13 V, and E_p^{ox} = 0.52 and 0.69 V. The CVs also show no overlap between the wave corresponding to Fe(II/III) and of the redox potentials of the Rh(I/II) and Rh(II/III) processes. The similitude of the Fe(II/III) redox potential values of the ferrocenylcarbene-substituents (the only waves that meet the criteria for a fully reversible system in our series) allow only in certain cases the data to be useful as a comparative tool to discriminate between the overall electronic effect of the more (aminocarbene) or less (ethoxycarbene) donating carbene ligands, and the co-ligands (cod; $(CO)_2$; CO, PR_3 (R = Ph, Cy or OPh) and CO, $AsPh_3$). For example, there is a significant difference of 0.11 V between E°′ observed for the Fe(II/III) redox potential values of **4** and its cod analogue **2** (which can be oxidized at lower potentials because it has a more donating ligand). However, the irreversible nature of the Rh(I/II) and Rh(II/III) processes (tabulated as E_p^{ox} in Table 3) means that a correlation between the LEPs and TEPs is impossible.

The irreversible reduction wave at negative potential corresponds to the one-electron reduction of the Rh=C bond to $^-$Rh-C$^\cdot$, similarly to the reduction of carbene ligands of Group 6 Fischer carbene complexes.[14b,16a] In this case, a clear qualitative trend of the overall electron withdrawing ability of the carbene ligand and the co-ligands can be established, corresponding to the trend observed for the IR carbonyl stretching frequencies of the complexes **1–8**. The reduction potentials can be arranged in order of decreasing negative values for **2** (cod, NH^nPr; -2.60 V) > **1** (cod, OEt; -2.42 V) > **6** (PCy_3, CO, OEt; -2.34 V) > **5** (PPh_3, CO, OEt; -2.30 V); **4** ($(CO)_2$, NH^nPr; -2.30 V) > **8** ($AsPh_3$, CO, OEt; -2.20 V) > **7** ($P(OPh)_3$, CO, OEt; -2.16 V) > **3** ((CO_2), OEt; -1.95 V) where the more electron withdrawing carbene and co-ligands display greater ease of reduction.

Hydroformylation of 1-octene. Complexes **1–8** were evaluated as catalyst precursors in the hydroformylation of 1-octene. The reaction conditions for **1** were optimized by variation of the syn-gas pressure (20–40 bar), temperature (70–90 °C) and reaction time (4–8 hrs). Under the optimized conditions of 40 bar and 80 °C, the catalyst precursors displayed excellent conversion (>99%) of 1-octene after 4 hours, as well as good chemoselectivity (85–100%) towards aldehydes (Table 4).Only moderate regioselectivity was observed with *n*/*iso*-aldehyde ratios ranging from 0.79–1.33, generally favoring the formation of linear aldehydes. A mercury drop-test was performed on catalyst **1** with no resulting significant change in either the conversion or chemo/regioselectivity of the catalyst, thereby indicating that a heterogeneous catalytic mode of action can be excluded.[26]

The TOF-values ranged from 343–418 h^{-1}, where the ethoxycarbene complexes consistently display higher activities than the analogous aminocarbene complexes **2** and **4.**

The effect of the donating capacity of the co-ligands also result in the general trend for activity (TOF) of the ferrocenylcarbene complexes, arranged in order of decreasing activity: $(CO)_2$ > CO, L (PR_3, $AsPh_3$) > cod. In contrast, the *n*/*iso*-selectivity (regioselectivity) displays the reversed trend, with *n*/*iso* (aminocarbene **2**, **4**) > *n*/*iso* (ethoxycarbene **1**, **3**), contrary to the expected improved selectivity for more electron-withdrawing carbene ligands. Again this trend is also reflected by the results obtained for complexes **5**–**8**, where the most donating phosphane co-ligand (PCy_3, **6**) display a higher *n*/*iso* ratio than for example **5** (PPh_3) or **7** ($P(OPh)_3$). However this observation should take into account the overall chemoselectivity, as the *n*/*iso*-ratio generally decreases as the total percentage of aldehyde formation increases.

Examples of very active [Rh(cod)X(NHC)] complexes as 1-octene hydroformylation catalyst precursors, with TOFs ranging from 480–3540 h^{-1},were reported by Weberskirch and co-workers,[27] however the selectivity decreased to *n*/*iso*-ratios of less than 0.50 close to full conversion due to olefin isomerization. In contrast, Trzeciak *et al.* reported excellent selectivities with *n*/*iso*-ratios in the range of 16–27 with the addition of phosphorous ligands to the [Rh(cod)Cl(NHC)] catalysts, but this occurred at the expense of low aldehyde yields of 18–26%.[28]Examples of dinuclear Rh-NHC complexes featuring a bridging bisNHC-pyridyl ligand showed full conversion to the aldehydes, but mostly branched aldehydes (86–100%) were obtained with TOF-values of 3.2–15.7 h^{-1}.[29]

To address the issue of the Rh-$C_{carbene}$ bond stability, a reaction similar to those proposed to test Rh-NHC bond stability was performed.[4d,26,29] A high pressure NMR-tube was charged with **1** (0.03 g, 0.06 mmol) and substrate 1-hexene (0.50 mmol, 0.6 mL) dissolved in C_6D_6 (0.70 mL).The reaction vessel was sequentially pressurized with CO (g) and H_2(g), and heated at 80°C for 8 hours. The immediate formation of **3** from **1** was observed (see Figure S20 (a), SI: $^{13}C\{^1H\}$ NMR δ 290.8 (d, *J* = 39.0 Hz, Rh-$C_{carbene}$), 188.2 (d, *J*= 49.8 Hz, Rh-CO) and 184.0 (d, *J* = 75.7 Hz, Rh-CO). After 8 hours of heating, a new carbene chemical shift, and a new broadened carbonyl ligand resonance were observed (Figure S20 (b), ^{13}C NMR δ 285.3 (d, *J* = 48.7 Hz, Rh-$C_{carbene}$), 185.2 (d, *J* = 92.2 Hz, Rh-CO). This result clearly evidences the retention of the Rh-$C_{carbene}$ bond, albeit a modified Rh-carbene carbonyl complex. Presumably, a dimeric Rh-carbene carbonyl complex[6a] is formed as only one new carbonyl and carbene carbon doublet is observed.

No upfield hydride resonances (up to -20 ppm) were observed in the ^1H NMR spectrum to support the formation of a catalytically active Rh(carbene)-hydrido species (analogous to the Wilkinson catalyst),[30] according to the underlying mechanism of hydroformylation.[27]

CONCLUSIONS

In this study, we achieved the synthesis and isolation of the novel ferrocenylcarbene complexes of rhodium(I) (**1**–**8**). Spectroscopic characterization to determine the carbonyl stretching frequencies of complexes **3**–**8**, and calculated TEP-values for **3** and **4** indicate the strongly donating effect of the ferrocenylcarbene substituent; and to a greater extent for the aminocarbene ligand of **4** compared to the alkoxy-analogue **3**. The expected trend for the co-ligands cod > CO, PCy_3 > CO, PPh_3 > CO, $AsPh_3$ > CO, $P(OPh)_3$ > $(CO)_2$ towards decreasing donor-ability was also confirmed by NMR and FT-IR spectroscopic results and cyclic voltammetry. The complexes **1**–**8** were screened as catalysts for the hydroformylation of 1-octene. Excellent conversion of the substrate olefins were observed, with turnover frequencies, chemo- and regioselectivity towards the linear aldehydes, comparable to results reported for rhodium NHC-complexes. Although the ferrocenyl substituent results in Fischer carbene ligands with electron donating abilities similar to NHCs, the Fischer carbene ligand is dissymmetric in contrast to typical NHCs and phosphines. Undoubtedly this steric effect also plays a role with regards to the selectivity of the precursor catalysts. Finally, the retention of the rhodium-carbene bond under hydroformylation conditions was confirmed in a $^{13}C\{^1H\}$ NMR spectroscopic study.

EXPERIMENTAL SECTION

General Procedures. The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry, oxygen-free dinitrogen or argon, using standard Schlenk techniques. All reaction mixtures were mechanically stirred and, where appropriate, the progress of a reaction was monitored by IR spectroscopy. The precursors $[Cr(CO)_5\{C(OEt)Fc\}]$[17]and $[Rh(cod)Cl]_2$[31]were prepared according to literature procedures. Silica gel 60 (particle size 0.0063-0.200 mm) was used as resin for all separation in column chromatography. Anhydrous tetrahydrofuran, diethyl ether and *n*-hexane were distilled over sodium metal and dichloromethane over CaH_2. All other reagents are commercially available and were used as received.

NMR spectra were recorded on Bruker Ultrashield Plus 400 AVANCE 3 and Bruker Ultrashield 300 AVANCE 3 spectrometers using $CDCl_3$ and C_6D_6 as solvents at 25°C. The NMR spectra were recorded for ^1H at 300.13 MHz, ^{13}C at 100.163 and 75.468 MHz and ^{31}P at 161.976 and 121.495 MHz. The chemicals shifts were recorded in ppm, using deuterated solvent signals for internal references. For $CDCl_3$ an C_6D_6 respectively, δH at 7.2600 and 7.1500 ppm, and δC at 77.360 and 128.000 ppm, and the $^{31}P\{^1H\}$ NMR spectra were referenced to the deuterated lock solvent which had been referenced to 85% H_3PO_4. Infrared spectroscopy was performed on a Perkin Elmer Spectrum RXI FT-IR spectrophotometer over the range 3400 to 1600 cm^{-1}. Solution IR spectra were recorded in CH_2Cl_2 using a NaCl cell with a path length of *ca.* 1.0 mm. Melting points were measured with a Stuart SMP10 melting point apparatus.

Most of the crystals were grown by slow diffusion of *n*-hexane into a concentrated CH_2Cl_2 solution of the metal complexes at 4ºC, except for those of[$Rh(CO)_2Cl${C(OEt)Fc}] **3** which required -30ºC. X-ray single crystal intensity data for **1**, **2**, **5** and **6** were collected at 120 K (**1**) or 150 K (**2**, **5** and **6**) on a Bruker D8 Venture diffractometer with a kappa geometry goniometer and a Photon 100 CMOS detector. Data for **4** were collected at 173 K on a Nonius diffractometer with a kappa geometry goniometer and CCD detector, and were scaled and reduced using *SAINT*[32] (**1**, **2**, **5** and **6**) or *DENZO-SMN*[33] (**4**). Absorption corrections were performed using SADABS.[32]The structures were solved by a novel duel-space algorithm using SHELXT[34] (**1**, **2**, **5** and **6**) or by direct methods (**4**) and were refined by full-matrix least-squares methods based on F^2 using SHELXL version 2014/7.[35] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except amine-H atoms were placed in idealized positions and refined using riding models. The amine-H atom positions in **2** and **4** were located and were refined. The N-H bond distance in **4** was constrained to 0.970(5)Å. In **6**, the chlorine and *trans* carbonyl ligands are disordered with the chlorine and carbonyl position interchanged. The site occupation factors refined to 0.8077(15) for the main orientation and 0.1923(15) for the flipped orientation. Mass spectral analyses were performed on a Synapt G2 HDMS by direct infusion at 5 µL/min with positive electron spray as the ionization technique. The *m/z* values were measured in the range of 400-1500 with acetonitrile as solvent. Elemental analyses were carried out using a Thermo Flash 1112 Series CHNS-O Analyzer. Following extensive drying, analyses of complexes **2**, **5** and **7–8** are outside acceptable limits and are ascribed to the presence of solvent molecules (CH_2Cl_2, *n*-hexane) and/or silicon grease. The full ^{1}H, ^{13}C (and where applicable, ^{31}P) NMR spectra are therefore included in the SI to attest to the purity of the compounds.

Electrochemical studies were carried out using Metrohm µAutolab type III potentiostat linked to a computer using GPES Electrochemistry software, in conjunction with a three-electrode cell. The working electrode was a glassy carbon disc (3.0 mm diameter) and the counter electrode was a platinum wire. The reference was a non-aqueous Ag/Ag^+electrode separated from the test solution by a fine porosity frit. Solutions in CH_2Cl_2 were 1.0×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in [N^nBu_4][PF_6] as the supporting electrolyte. Under these conditions, $E^{\circ\prime}$ for the redox couple [Fe(η-$C_5Me_5)_2$]$^{o/1+}$, added to the test solutions as internal standard, is -0.54 V. All E_p^{ox}, E_p^{red} and $E^{\circ\prime}$values are at scan rates of 100 mV s^{-1}.

The new metal complexes prepared are stable under nitrogen and dissolve in solvents such as dichloromethane, chloroform or benzene to give air-sensitive solutions.

General procedure for the hydroformylation experiments. Hydroformylation reactions were conducted (in triplicate) in a 90 mL stainless steel pipe reactor. In a typical experiment, the catalyst precursor (**1—8**) (0.0039 mmol), substrate 1-octene (721.0 mg, 6.37 mmol), and the internal standard, *n*-decane (180.0 mg, 1.26 mmol), were dissolved in toluene (5.0 mL) and transferred into a stainless steel pipe reactor (90 mL). The air-tight reactor was then deaerated by flushing three times with N_2 gas, twice with syngas, then pressurized with syngas (1:1, CO:H_2 ratio) and heated to the desired temperature and pressure. After the reaction time, the reactor was depressurized and the reaction mixture transferred for cooling. The samples were analyzed by gas chromatography and the products were confirmed in relation to authentic *iso*-octenes and aldehydes.

Syntheses of complexes 1–8.

[Rh(cod)Cl{C(OEt)Fc}] 1. A mixture of [$Cr(CO)_5${C(OEt)Fc}] (1.67 g, 3.84 mmol) and [Rh(cod)Cl]$_2$ (0.946 g, 1.92 mmol) in CH_2Cl_2 (30 mL) was stirred for 14 days at room temperature. The formation of unknown byproducts can be observed by TLC if the temperature is increased. The resulting dark red solution was reduced in volume *in vacuo* and then added to a silica chromatography column. Elution with CH_2Cl_2 gave a deep red band which was collected and evaporated to dryness. The product, a dark red oil, was dissolved in 3 mL of CH_2Cl_2 and treated with *n*-hexane (5 mL) to precipitate a crystalline red solid. Yield = 0.89 g, 95%. Mp: 110–111ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (dq, ^2J(HH) = 10.4, ^3J(HH) = 7.2 Hz, 1H, O<u>CH_2</u>CH_3), 5.51 (dq, ^2J(HH) = 10.4 Hz, ^3J(HH) = 7.1 Hz, 1H, O<u>CH_2</u>CH_3), 5.41 (dd, ^3J(HH) = 1.3 Hz, ^4J(HH) = 1.3 Hz, 1H, FeCp'), 5.38–5.32 (m, 1H, cod –<u>CH</u>), 5.21–5.14 (m, 1H, cod –<u>CH</u>), 4.83 (dd, ^3J(HH) = 1.3 Hz, ^4J(HH) = 1.3 Hz, 1H, FeCp'), 4.79–4.76(m, 1H, FeCp'), 4.66–4.64 (m, 1H, FeCp'), 4.39 (s, 5H, FeCp), 3.38–3.32 (m, 1H, cod –<u>CH</u>), 3.24–3.17 (m, 1H, cod –<u>CH</u>), 2.60–1.90 (m, 8H, cod-<u>CH_2</u>), 1.65 (t, ^3J(HH) = 7.1 Hz, 3H, OCH_2<u>CH_3</u>).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 309.2 (d, ^1J(RhC) = 43.2 Hz, $C_{carbene}$), 107.5 (d, ^1J(RhC) = 4.6 Hz, cod-<u>CH</u>), 107.1 (d, ^1J(RhC) = 4.5 Hz, cod-<u>CH</u>), 86.7 (d, ^2J(RhC) = 2.1 Hz, FeCp'-C_{ipso}), 78.3 (O<u>CH_2</u>CH_3), 75.4 (FeCp'), 74.8 (FeCp'), 73.8 (d, ^1J(RhC) = 14.9 Hz, cod-<u>CH</u>), 73.7 (FeCp'), 70.6 (FeCp), 69.7 (FeCp'), 68.0 (d, ^1J (RhC) = 14.9 Hz, cod-<u>CH</u>), 33.7 (cod-<u>CH_2</u>), 32.4 (cod-<u>CH_2</u>), 29.0 (cod-<u>CH_2</u>), 27.9 (cod-<u>CH_2</u>), 15.8 (OCH_2<u>CH_3</u>).

Anal. Calcd. For $C_{21}H_{26}OClFeRh$: C 51.62, H 5.36. Found: C 51.99, H 4.94. ESI-HRMS (15 V, positive mode, *m/z*): calcd. for $[M-Cl]^+$ 453.0388; found, 453.0357.

[Rh(cod)Cl{C(NH^{n}Pr)Fc}] 2. To a dark red solution of **1** (0.149 g, 0.30 mmol) in 10 mL of Et_2O, $^nPrNH_2$ (0.05 mL, 0.60 mmol) was added dropwise at room temperature. The mixture was stirred for 2 hours, during which period the yellow-orange product **2**slowly precipitated out of solution. The solvent was decanted and the solid obtained washed with *n*-hexane (20 mL) and dried *in vacuo*. Yield =0.120 g, 75%. Mp (decomp.): 164–167ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, br, 1H, <u>NH</u>$CH_2CH_2CH_3$), 5.18 (s, br, 1H, FeCp'), 5.15–5.08 (m, 1H, cod-<u>CH</u>), 5.02–4.95 (m, 1H, cod-<u>CH</u>), 4.74 (s, br, 1H, FeCp'), 4.56 (s, br, 1H, FeCp'), 4.49 (s, br, 1H, FeCp'), 4.52–4.36 (m, 3H, NH<u>CH_2</u>CH_2CH_3), 4.26 (s, 5H, FeCp), 3.41–3.35 (m, 1H, cod-<u>CH</u>), 3.28–3.22 (m, 1H, cod-<u>CH</u>), 2.56–1.77 (m, 10H, cod-<u>CH_2</u>, NHCH_2<u>CH_2</u>CH_3), 1.12 (t, ^3J(HH) = 7.4 Hz, 3H, NHCH_2CH_2<u>CH_3</u>). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 257.9 (d, ^1J(RhC) = 40.1 Hz, $C_{carbene}$), 100.9 (d, ^1J(RhC) = 6.1 Hz, cod-<u>CH</u>), 100.8 (d, ^1J(RhC) = 7.3 Hz, cod-<u>CH</u>), 83.6 (FeCp'-C_{ipso}), 72.4 (FeCp'), 72.1 (FeCp'), 71.6 (FeCp'), 71.0 (d, ^1J(RhC) = 15.2 Hz, cod-<u>CH</u>), 70.4 (FeCp), 68.7 (FeCp'), 68.4 (d, ^1J(RhC) = 15.0 Hz, cod-<u>CH</u>), 56.1 (NH<u>CH_2</u>CH_2CH_3), 33.9 (cod-<u>CH_2</u>), 32.3 (cod-<u>CH_2</u>), 29.5 (cod-<u>CH_2</u>), 28.4 (cod-<u>CH_2</u>), 23.5 (NHCH_2<u>CH_2</u>CH_3), 11.9 (NHCH_2CH_2<u>CH_3</u>. (IR, CH_2Cl_2, ν(NH), cm^{-1}): 3320. Anal. Calcd. For $C_{22}H_{29}NClFeRh$ + 0.06 eq CH_2Cl_2: C 50.53, H 5.49, N 2.64. Found: C 51.18, H 5.23, N 2.19. ESI-HRMS (15 V, positive mode, *m/z*): calcd. for $[M-Cl]^+$ 466.0704; found, 466.0718.

[$Rh(CO)_2$Cl{C(OEt)Fc}] 3. Carbon monoxide gas was bubbled for 5 min through a stirred solution of **1** (0.139 g, 0.28 mmol) in CH_2Cl_2 (5 mL) in the absence of light and at -10ºC. Immediate colour change from deep red to dark purple was observed. The flow of CO was stopped and purple needle-like crystals of the

product were grown by slow diffusion of *n*-hexane (5 mL) into the concentrated CH_2Cl_2 reaction mixture at -30 °C. Yield = 0.079 g,65%. Mp (decomp.): 120–122°C.^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 (q, br, ^3J(HH) = 6.8 Hz, 2H, O$\underline{CH_2}CH_3$), 5.20 (s, br, 1H, FeCp'), 5.14 (s, br, 1H, FeCp'), 5.01 (s, br, 2H, FeCp'), 4.44 (s, 5H, FeCp), 1.59 (t, ^3J(HH) = 7.1 Hz, 3H, OCH$_2\underline{CH_3}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 289.3 (d, ^1J(RhC) = 37.9 Hz, $C_{carbene}$), 186.5 (d, ^1J(RhC) = 49.5 Hz, CO), 182.8 (d, ^1J(RhC) = 77.4 Hz, CO), 85.6 (d, ^1J(RhC) = 2.1 Hz FeCp-C_{ipso}), 80.6 (O$\underline{CH_2}$CH$_3$), 77.2 (FeCp'), 77.0 (FeCp'), 74.7 (FeCp'), 71.2 (FeCp), 70.5 (FeCp'), 14.8 (OCH$_2\underline{CH_3}$). (IR, CH_2Cl_2, ν(CO), cm^{-1}): 2001, 2084. Anal. Calcd. For $C_{15}H_{14}O_3ClFeRh$: C 41.28, H 3.23. Found: C 41.39, H 2.88. ESI-MS (15 V, positive mode, *m*/*z*): calcd. for [M-Cl-CO]$^+$ 372.9398; found, 372.9282.

The complex **[Rh(CO)$_2$Cl{C(NH^{n}Pr)Fc}] 4** was prepared similarly from **2** (0.105 g, 0.21 mmol), but at room temperature. In this case, no visible colour change was observed upon CO bubbling. Slow addition of *n*-hexane to the reaction mixture allowed a dark orange powder, which was washed with *n*-hexane (10 mL) and dried *in vacuo*.Yield = 0.08 g, 84%. Mp (decomp): 138–139°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, br, 1H, $\underline{NH}CH_2CH_2CH_3$), 5.09 (s, br, 1H, FeCp'), 4.91 (s, br, 1H, FeCp'), 4.62 (s, br, 2H, FeCp'), 4.29 (s, 5H, FeCp), 4.13 (s, br, 1H, NH$\underline{CH_2}$CH$_2$CH$_3$), 3.54 (s, br, 1H, NH$\underline{CH_2}$CH$_2$CH$_3$), 1.81–1.68 (m, 2H, NHCH$_2\underline{CH_2}$CH$_3$), 1.01 (t, ^3J(HH) = 7.4 Hz, 3H, NHCH$_2$CH$_2\underline{CH_3}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 237.8 (d, ^1J(RhC) = 34.7 Hz, $C_{carbene}$), 186.9 (d, ^1J(RhC) = 51.3 Hz, CO), 184.2 (d, ^1J(RhC) = 78.2 Hz, CO), 83.0 (FeCp'-C_{ipso}), 73.6 (FeCp'), 70.5 (FeCp), 67.5 (FeCp'), 56.9 (NH$\underline{CH_2}$CH$_2$CH$_3$), 22.9 (NHCH$_2\underline{CH_2}$CH$_3$), 11.5 (NHCH$_2$CH$_2\underline{CH_3}$). (IR, CH_2Cl_2, ν(CO) and ν(NH), cm^{-1}): 1995, 2077, 3315.Anal. Calcd. For $C_{16}H_{18}NO_2ClFeRh$: C 42.66, H 4.03, N 3.11. Found: C 42.55, H 3.83, N 3.41. ESI-HRMS (15V, positive mode, *m*/*z*): calcd. for [M-Cl-CO]$^+$385.9714; found, 385.9647.

[Rh(CO)(PPh$_3$)Cl{C(OEt)Fc}] 5. Carbon monoxide gas was bubbled for 5 min through a stirred solution of **1**(0.215 g, 0.44 mmol) in CH_2Cl_2(10 mL) in the absence of light at -10 °C. The flow of CO was stopped and the solution allowed to reach room temperature. Solid PPh_3 (0.116 g, 0.44 mmol) was then added and the mixture stirred for 5 minutes. Slow concentration of the mixture of the filtrate and *n*-hexane under reduced pressure gave a purple-red solid. Yield = 0.265 g, 83%. Mp: 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 6H, PPh_3), 7.42–7.39 (m, 9H, PPh_3), 5.73 (dq, ^2J(HH) = 10.5 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.52 (dq, ^2J(HH) = 10.5 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.40 (s, br, 1H, FeCp'), 5.16 (s, br, 1H, FeCp'), 4.87 (dd, ^1J(HH) = 3.9, ^2J(HH) = 2.4 Hz, 2H, FeCp'), 4.39 (s, 5H, FeCp), 1.65 (t, ^3J(HH) = 7.2 Hz, 3H, OCH$_2\underline{CH_3}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 299.7 (dd, ^2J(PC) = 110.2 Hz, ^1J(RhC) 40.1 Hz, $C_{carbene}$), 187.5 (dd, ^1J(RhC) = 81.4 Hz, ^2J(PC) = 16.2 Hz, CO), 134.9 (d, ^1J(PC) = 11.9 Hz, PPh_3-C_{ipso}), 134.0 (d, ^2J(PC)= 38.3 Hz, PPh_3), 130.2 (PPh_3), 128.48 (d, ^3J(PC) = 9.7 Hz, PPh_3), 87.3 (dd, ^2J(RhC) = 8.2, ^3J(PC) = 2.3 Hz, FeCp'-C_{ipso}), 79.9 (O$\underline{CH_2}$CH$_3$), 75.9 (FeCp'), 75.3 (FeCp'), 70.8 (FeCp), 15.23 (OCH$_2\underline{CH_3}$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 27.4 (d, ^1J(RhP) = 99.9 Hz). (IR, CH_2Cl_2, ν(CO), cm^{-1}): 1965.Anal. Calcd. For $C_{32}H_{29}O_2PClFeRh$: C 57.30, H 4.36. Found: C 56.47, H 4.27. ESI-HRMS (15 V, positive mode, *m*/*z*): calcd. for [M-Cl-PPh$_3$]$^+$ 372.9398; found, 372.9416. The analogues **[Rh(LL)Cl{C(XR)Fc}] [LL = (CO, PR$_3$) (R = Cy or OPh)** and **(CO, AsPh$_3$); XR = OEt] 6–8** were prepared similarly as purple-red powders (**6**, or as oily solids **7**, **8**).

[Rh(CO)(PCy$_3$)Cl{C(OEt)Fc}] 6. Yield = 0.102 g, 65%. Mp: 167–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (dq, ^2J(HH) = 10.5 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.42 (dq, ^2J(HH) = 10.6 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.31 (s, br, 1H, FeCp'), 5.10 (s, br 1H, FeCp'), 4.81 (dd, ^2J(HH) = 2.6 Hz, ^2J(HH) = 2.6 Hz, 2H, FeCp'), 4.38 (s, 5H, FeCp), 2.26 – 2.16 (m, 3H, PCy_3), 2.07 – 2.03 (m, 6H, PCy_3), 1.83–1.60 (m, 15H, PCy_3), 1.62 (t, ^3J(HH) = 7.2 Hz, 3H, OCH$_2\underline{CH_3}$), 1.29 (s, 9H, PCy_3).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 302.5 (dd, ^2J(PC) = 103.2 Hz, ^1J(RhC) = 38.9 Hz. $C_{carbene}$), 188.0 (dd, ^1J(RhC) = 82.3 Hz, ^2J(PC) = 16.7 Hz, CO), 87.6 (dd, ^2J(RhC) = 7.5 Hz, ^3J(PC) = 2.5 Hz, FeCp'-C_{ipso}), 78.7 (O$\underline{CH_2}$CH$_3$), 75.1 (FeCp'), 74.5 (FeCp'), 70.3 (FeCp), 33.4 (d, ^1J(PC) = 17.7 Hz, PCy_3-C_{ipso}), 30.3 (PCy_3), 27.8 (PCy_3), 27.7 (PCy_3), 26.7 (PCy_3), 14.9 (OCH$_2\underline{CH_3}$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 34.7 (d, ^1J(RhP) = 98.4 Hz). (IR, CH_2Cl_2, ν(CO), cm^{-1}): 1946. Anal. Calcd. For $C_{32}H_{47}O_2PClFeRh$ + 0.33 eq C_6H_{14}: C 56.91, H 7.26. Found: C 56.41, H 6.57. ESI-HRMS (15 V, positive mode, *m*/*z*): calcd. for [M-Cl-CO]$^+$ 625.1769; found, 625.1733; calcd. for [M-Cl-PCy$_3$]$^+$ 372.9398; found, 372.9416.

[Rh(CO)(P(OPh)$_3$)Cl{C(OEt)Fc}] 7. Yield = 0.163 g, 63%. Mp: 74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, ^2J(HH) = 7.8 Hz, ^3J(HH) = 7.8 Hz, 6H, OPh_3), 7.37 (dd, ^2J(HH) = 7.9 Hz, ^2J(HH) = 7.9 Hz, 6H, OPh_3), 7.19 (dd, ^2J(HH) = 8.1 Hz, ^3J(HH) = 8.1 Hz, 3H, OPh_3), 5.06 (q, ^3J(HH) = 7.1 Hz, 2H, O$\underline{CH_2}$CH$_3$), 4.88–4.87 (m, 2H, FeCp'), 4.83 – 4.80 (m, 2H, FeCp'), 4.38 (s, 5H, FeCp), 1.41 (t, ^3J(HH) = 7.2 Hz, 3H, OCH$_2\underline{CH_3}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 298.4 (dd, ^2J(PC) = 174.1 Hz, ^1J(RhC) = 38.9 Hz, $C_{carbene}$), 184.8 (dd, ^1J(RhC) = 79.1 Hz, ^2J(PC) = 21.0 Hz, CO), 151.9 (d, ^2J(PC) = 4.8 Hz, OPh_3-C_{ipso}), 129.8 (OPh_3), 125.0 (OPh_3), 122.2 (d, ^3J(PC) = 5.5 Hz, OPh_3), 86.5 (dd, ^2J(RhC) = 12.6 Hz, ^3J(PC) = 2.5 Hz, FeCp'-C_{ipso}), 79.9 (O$\underline{CH_2}$CH$_3$), 76.3 (FeCp'), 75.9 (FeCp'), 71.0 (FeCp), 15.0 (OCH$_2\underline{CH_3}$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 127.0 (d, ^1J(RhP) = 177.4 Hz).(IR, CH_2Cl_2, ν(CO), cm^{-1}): 1986.Anal. Calcd. For $C_{32}H_{29}O_5PClFeRh$: C 53.47, H 4.07. Found: C 48.19, H 3.77. ESI-HRMS (15 V, positive mode, *m*/*z*): calcd. for [M-Cl-CO]$^+$ 655.0208; found, 655.0435; calcd. for [M-Cl-P(OPh)$_3$]$^+$ = 372.9398; found, 372.9282.

[Rh(CO)(AsPh$_3$)Cl{C(OEt)Fc}] 8. Yield = 0.096 g, 63%. Mp: 98–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, ^3J(HH) = 3.6 Hz, ^3J(HH) = 3.6 Hz, 6H, $AsPh_3$), 7.41 – 7.40 (m, 9H, $AsPh_3$), 5.75 (dq, ^2J(HH) = 10.4 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.57 (dq, ^2J(HH) = 10.2 Hz, ^3J(HH) = 7.2 Hz, 1H, O$\underline{CH_2}$CH$_3$), 5.40 (s, br, 1H, FeCp'), 5.21 (s, br, 1H, FeCp'), 4.87 (s, br, 2H, FeCp'), 4.41 (s, 5H, FeCp), 1.66 (t, ^3J(HH) = 7.1 Hz, 3H, OCH$_2\underline{CH_3}$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 295.3 (d, ^1J(RhC) = 45.1 Hz, $C_{carbene}$), 186.5 (d, ^1J(RhC) = 80.3 Hz, CO), 135.5 ($AsPh_3$), 134.4 ($AsPh_3$), 129.9 ($AsPh_3$), 129.0 ($AsPh_3$), 87.4(d, ^2J(RhC) = 3.5 Hz, FeCp'-C_{ipso}), 80.1 (O$\underline{CH_2}$CH$_3$), 75.8 (FeCp'), 75.4 (FeCp'), 70.9 (FeCp), 15.2 (OCH$_2\underline{CH_3}$). (IR, CH_2Cl_2, ν(CO), cm^{-1}): 1966.Anal. Calcd. For $C_{32}H_{29}O_2AsClFeRh$: C 53.78, H 4.09. Found: C 51.71, H 3.52.ESI-HRMS (15 V, positive mode, *m*/*z*): calcd for [M-Cl-AsPh)$_3$]$^+$ = 372.9398; found, 372.9282.

ASSOCIATED CONTENT

Supporting Information

Figures giving the NMR spectra of complexes **1–8** and a table giving the X-ray crystallographic collection data and parameters for **1**, **2** and **4–6** (also in CIF format) are available free of charge on the ACS Publications website in PDF format.

AUTHOR INFORMATION

Corresponding Author

* daniela.bezuidenhout@up.ac.za (D.I.B.)

Notes

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors gratefully acknowledge Dr Shankara G. Radhakrishnan, University of Pretoria, for valuable discussions with regards to the cyclic voltammetry experiments.
This work was supported by funding from the National Research Foundation,South Africa (D.I.B., Grant numbers 87890, 92521 and 92581) and Sasol Technology R&D Pty. Ltd., South Africa (D.I.B.), and the NRF-DST Centre of Excellence in Catalysis (c* change) (G.S.S.). A generous loan of rhodium trichloride hydrate from Johnson Matthey/AngloAmerican Platinum Ltd. Corporation is gratefully acknowledged.

REFERENCES

(1) For reviews on Rh-catalyzed hydroformylation, see:(a) Whiteker, G. T.; Cobley, C.J. Organometallics as Catalysts in the Fine Chemical Industry. In *Topics in Organometallic Chemistry,* Beller, M.; Blaser, H.-U., Eds.; Vol. 42, Springer-Verlag, Berlin, **2012**, pp35–46. (b) Gual, A.; Godard, C.; Castillon, S.; Claver, C. *Tetrahedron: Asymmetry,* **2010**, *21*, 1135–1146. (c) Lazzaroni, R.; Settambolo, R.; Alagona, G.; Ghio, C. *Coord. Chem. Rev*. **2010**, *254*, 696–706. (d) Breit, B. Directed metallation. In *Topics in Organometallic Chemistry,* Chatani, N., Ed.; Vol 24, Springer-Verlag, Berlin, **2007**, pp145–168. (e) Kamer, P.C.J.; Reek, J.N.H.; van Leeuwen, P.W.N.M. Rhodium Catalyzed Hydroformylation,in *Mechanisms in Homogeneous Catalysis,* Heaton, B., Ed.; Wiley-VCH Verlag GmbH & Co. kGaA: Weinheim, **2005**, 231–269. (f) van Leeuwen, P.W.N.M.; Claver, C., Eds. *Rhodium Catalyzed Hydroformylation,* Kluwer Academic Publishers, Dordrecht, **2000**. (g) Trzeciak, A.M.; Ziólkowski, J.J.; *Coord. Chem. Rev*. **1999**, *190–192*, 883–900.
(2) Selected recent reviews on NHCs and references therein: (a) Jahnke, M.C.; Hahn, F.E. *Chem. Lett*. **2015**, *44*, 226–237. (b) Hopkinson, M.N.; Richter, C.; Schedler, M.; Glorius, F. *Nature*, **2014**, *510*, 485–496. (c) Nelson, D.J.; Nolan, S.P. *Chem. Soc. Rev.* **2013**, *42*, 6723–6753. (d) Hahn, F.E. Jahnke, M.C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172. (e) N-heterocyclic carbenes in transition metal catalysis. In Topics in Organometallic Chemistry, Glorius, F. Ed.; Springer-Verlag, Berlin/Heidelberg, **2007**. (f) N-Heterocyclic carbenes in Synthesis, Nolan, S.P., Ed.; Vol. 42, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2006**, pp 1–20. (g) Crudden, C.M.; Allen, D.P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.
(3)(a) Dröge, T.; Glorius, F. *Angew. Chem. Int. Ed*. **2010**, *49*, 6940-6952. (b) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev*. **2007**, *251*, 874–883.
(4) Recent reviews on Rh-NHC complexes for hydroformylation, and references therein: (a) Gil, W.; Trzeciak, A.M. *Coord. Chem. Rev*. **2011**, *255*, 473–483. (b) Almeida, A.R.; Peixoto, A.F.; Calvete, M.J.F.; Gois, P.M.P.; Pereira, M.M. *Curr. Org. Synth*. **2011**, *8*, 764–775. (c) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev*. **2009**, *109*, 3612–3676. (d) Praetorius, J.M.; Crudden, C.M. *Dalton Trans*. **2008,** 4079–4094. (e) Veige, A.S. *Polyhedron* **2008**, *27*, 3177–3189. (f) Peris, E.; Crabtree, R.H. *Coord. Chem. Rev*. **2004**, *248*, 2239–2246.
(5) Selected recent reviews on Fischer carbene complexes, and references therein: (a) Raubenheimer, H.G. *Dalton Trans*. **2014**, *43*, 16959–16973. (b) Herndon, J.W. *Coord. Chem. Rev*., **2013**, 286, 30–150. (c) Bezuidenhout, D.I.; Lotz, S.; Liles, D.C.; van der Westhuizen, B. *Coord.Chem. Rev.* **2012**, *256*, 479–524. (d) Strassner, T. Metal Carbenes in Organic Synthesis. In *Topics in Organometallic Chemistry,* Dötz, K.H., Ed.; Vol. 13, Springer-Verlag, Berlin, **2004**.
(6) (a) Barluenga, J.; Vicente, R.; López, L.A.; Tomás, M. *J. Organomet. Chem*. **2006**, *691*, 5642–5647. (b) Barluenga, J.; Vicente, R.; López, L.A.; Rubio, E.; Tomás, M.; Álvarez-Rúa, C. *J. Am. Chem. Soc*. **2004**, *126*, 470–471. (c) Göttker-Schnetmann, I.; Aumann, R.; Bergander, K. *Organometallics* **2001**, *20*, 3574–3581. (d) Motoyama, Y.; Shimozono, K.; Aoki, K.; Nishiyama, H. *Organometallics* **2002**, *21*, 1684–1696. (e) Erker, G.; Mena, M.; Hoffmann, U.; Menjon, B. *Organometallics* **1991**, *10*, 291–298. (f) Erker, G.; Lecht, R.; Tsay, Y.H.; Kruger, C. *Chem. Ber*. **1987**, *120*, 1763–1765 (g) Barger, P.T.; Bercaw, J.E. *Organometallics,* **1984**, *3*, 278–284.
(7) (a) López-Alberca, M.P.; Fernández, I.; Mancheño, M.J.; Gómez-Gallego, M.; Casarrubios, L.; Sierra, M.A. *Eur. J. Org. Chem*., **2011**, 3293–3300. (b) Barluenga, J.; Vicente, R.; López, L.A.; Tomás, M. *Tetrahedron* **2010**, *66*, 6335–6339. (c) Barluenga, J.; Vicente, R.; López, L.A.; Tomás, M. *J. Am. Chem. Soc.* **2006**, *128*, 7050–7054. (d) Barluenga, J.; Vicente, R.; López, L.A.; Tomás, M. *Tetrahedron* **2005**, *61*, 11327–11332.
(8) (a) Göttker-Schnetmann, I.; Aumann, R. *Organometallics* **2001**, *20*, 346–354. (b) Barluenga, J.; Vicente, R.; López, L.A.; Rubio, E.; Tomás, M.; Álvarez-Rúa, C. *J. Am. Chem.Soc.* **2004**, *126*, 470–471.
(9) Fernández-Rodríguez, M.A.; García-García, P.; Aguilar, E. *Chem. Commun*. **2010**, *46*, 7670–7687.
(10) (a) Hetterscheid, D.G.H.; Chikkali, S.H.; de Bruin, B.; Reek, J.N.H. *Chem.Cat.Chem*. **2013**, *5*, 2785–2795. (b) van der Vlugt, J. L. *Eur. J. Inorg. Chem*. **2012**, 363–375. (c) Liu, S.; Motta, A.; Delferro, M.; Marks, T.J. *J. Am. Chem. Soc*. **2013**, *135*, 8830–8833. (d) Siangwata, S.; Baartzes, N.; Makhubela, B.C.E.; Smith, G.S. *J. Organomet. Chem.* **2015**, *796*, 26–32.
(11) (a) Sierra, M. A.; Mancheño, M. J.; Sáenz, E.; del Amo, J. C.; *J. Am. Chem. Soc.* **1998**, *120*, 6812–6813. (b) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M.; *J. Am. Chem. Soc.* **2001**, *123*, 851–861.
(12) Sakurai, H.; Tanabe, K.; Narasaka, K.; *Chem. Lett*. **1999**, 75–75.
(13) Göttker-Schnetmann, I.; Aumann, R.; Bergander, K. *Organometallics***2001**, *20*, 3574–3581.
(14) (a) Connor, J. A.; Llyod, J. P. *J. Chem. Soc., Dalton Trans*., **1972**, *14*, 1470–1476. (b) van der Westhuizen, B.; Swarts, P. J.; Strydom, I.; Liles, D. C.; Fernández, I.; Swarts, J. C.; Bezuidenhout, D. I. *Dalton Trans*. **2013**, *42*, 5367–5378.
(15) Fernández, I.; Mancheño, M. J.; Vicente, R.; López, L. A.; Sierra, M. A. *Chem. Eur. J*. **2008**, *14*, 11222–11230.
(16) (a) Bezuidenhout, D. I.; Fernández, I.; van der Westhuizen, B.; Swarts, P. J.; Swarts, J. C. *Organometallics* **2013**, *32*, 7334–7344. (b) Bezuidenhout, D. I.; Barnard, W.; van der Westhuizen, B.; van der Watt, E.; Liles, D. C. *Dalton Trans.*, **2011**, *40*, 6711–6721. (c) Bezuidenhout, D. I.; van der Watt, E.; Liles, D. C.; Landman, M.; Lotz, S. *Organometallics* **2008**, *27*, 2447–2456.
(17) Connor, J. A.; Jones, E. M.; Lloyd, J. P. *J. Organomet. Chem.* **1970**, *24*, C20–C22.

(18) Bezuidenhout, D. I.; Liles, D. C.; van Rooyen, P. H.; Lotz, S. *J. Organomet. Chem.* **2007**, *692*, 774–783.
(19) Van der Westhuizen, B.; Swarts, P. J.; van Jaarsveld, L. M.; Liles, D. C.; Siegert, U.; Swarts, J. C.; Fernández, I.; Bezuidenhout, D. I. *Inorg. Chem.* **2013**, *52*, 6674–6684.
(20) For a definition of *syn*/*anti* conformers, see: (a) Fernández, I.; Cossío, F. P.; Arrieta, A.; Lecea, B.; Mancheño, M. J.; Sierra, M. A. *Organometallics* **2004**, *23*, 1065–1071. (b) Andrada, D. M.; Zoloff-Michoff, M. E.; Fernández, I.; Granados, A. M.; Sierra, M. A. *Organometallics* **2007**, *26*, 5854–5858. (e) Valyaev, D. A.; Brousses, R.; Lugan, N.; Fernández, I.; Sierra, M. A. *Chem.–Eur.* J. **2011**, *17*, 6602–6605. (f) Lugan, N.; Fernández, I.; Brousses, R.; Valyaev, D. A.; Lavigne, G.; Ustynyukd, N. A. *Dalton Trans*. **2013**, *42*, 898–901.
(21) Tolman, C. A. *Chem. Rev*. **1977**, *77*, 313–348.
(22) (a) Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663–1667. (b) Kelly, R. A., III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Smardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202–210.
(23) Wolf, S.; Plenio, H. *J. Organomet. Chem.***2009**, *694*, 1487–1492.
(24) Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem*. **1996**, *35*, 1013–1023.
(25) (a) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648–5656. (b) Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem*. **2001**, *40*, 5806–5811. (c) Collins, M. S.; Rosen, E. L.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2010**, *29*, 3047–3053.
(26)(a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855–859. (b) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A* **2003**, *198*, 317–341.
(27) Bortenschlager, M.; Schutz, J.; von Preysing, D.; Nuyken, O.; Herrmann, W. A.; Weberskirch, R. *J. Organomet. Chem.* **2005**, *690*, 6233–6237.
(28) Gil, W.; Trzeciak, A.M.; Ziólkowski, J.J. *Organometallics* **2008**, *27*, 4131–4138.
(29) Poyatos, M.; Uriz, P.; Mata, J.A.; Claver, C.; Fernández, E.; Peris, E. *Organometallics* **2003**, *22*, 440–444.
(30) Cauzzi, D.; Costa, M.; Gonsalvi, L.; Pellinghelli, M.A.; Predieri, G.; Tiripicchio, A.; Zanoni, R. *J. Organomet. Chem.* **1997**, *541*, 377–389.
(31) Giordano, G.; Crabtree, R. H.; Heintz, R.M.; Forster, D.; Morris, D.E. Low-valent complexes of Rh, Ir, Ni, Pd, and Pt, in *Inorganic Syntheses,* Angelici, R.J., Ed.; Wiley & Sons, Inc. New York, **1991**, Vol. 28, pp 88–89.
(32) *APEX2, (including SAINT and SADABS),* Bruker AXS Inc., Madison, WI, 2015.
(33) Otwinowski, Z.; Minor, W. Methods in Enzymology in *Macromolecular Crystallography*, Carter Jr, C. W.; Sweet, R. M., Eds.; vol. 276, Part A, Academic Press, **1997**, pp 307–326.
(34) Sheldrick, G. M. *Acta Cryst*. **2015**, *A71*, 3–8.
(35) Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3–8.

Graphic entry for Table of Contents (TOC)