

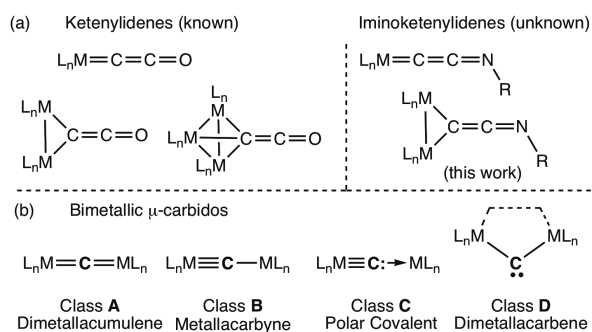
Construction of an Iminoketenylidene

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The new isonitrile- μ -carbido complexes [WPt(μ -C)Br(CNR)(PPh₃)(CO)₂(Tp*)] (R = C₆H₂Me₃-2,4,6, C₆H₃Me₂-2,6; Tp* = hydrotris(dimethylpyrazolyl)borate) rearrange irreversibly in polar solvents to provide the first examples of iminoketenylidene (CCNR) complexes.

Ketenylidene, CCO, belongs to an august group of molecules (CS, CH, CNH, NS, CP *etc.*) that, whilst not isolable in condensed phases, serve as stable ligands to transition metals. Despite being familiar to galactochemists,¹ back on planet earth linear (C_{∞v}) triplet ketenylidene remains elusive as a free molecule but has been observed within the mononuclear complexes [WCl₂(=C=C=O)(CO)(PMePh₂)₂]^{2a,b} and [M(=C=C=O)-(OSi^tBu₃)₃] (M = Nb, Ta)^{2c} in addition to a variety of polynuclear clusters.³ The organometallic chemistry of isonitriles (CNR) in many respects mimics that of carbon monoxide (CO) such that one might by extension consider the viability of iminoketenylidene (CCNR) ligands. Neither the free molecules nor their complexes have been previously described, although a small number of *iminoketenyl* complexes L_nM–C(CNR)R' are known.⁴ We report herein that the first examples of coordinated iminoketenylidene complexes arise from the unprecedented coupling of isonitrile and μ -carbido ligands.

Binuclear μ -carbido complexes comprise four distinct classes **A–D** (Scheme 1)^{5–8} with those from Class **B** (metallacarbynes) having the added intrigue of requiring disparate metal centres and M–C bond multiplicities. The thermally robust Class **B** carbido complex [WPt(μ -C)Br(PPh₃)₂(CO)₂(Tp*)] (**1**, Tp* = hydrotris(dimethylpyrazolyl)borate)^{6d} is readily obtained in good yield (77%) *via* oxidative addition of the bromocarbene [W(=CBr)(CO)₂(Tp*)] (**2**)^{6c} to

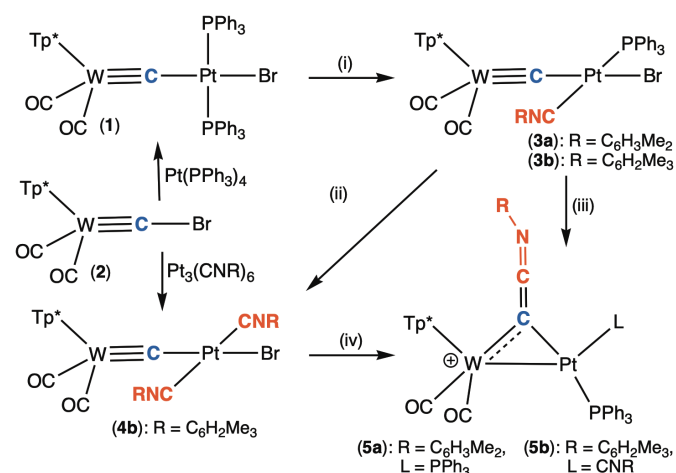


Scheme 1: a) Ketenylidene and Iminoketenylidene ligands. b) μ -carbido classification.^{5–8}

[Pt(PPh₃)₄].^{6k,l} Complex **1** affords access to a wide range of new carbido complexes *via* ligand substitution reactions at the platinum centre.^{6l} To explore the effect that π -acidic co-ligands might have on the W=C–Pt spine we have now addressed the synthesis of isonitrile-substituted analogues of **1**. The only previously described isonitrile carbido complex is [MoFe(μ -C)(CN^tBu)₂(CO)₂(η -C₅H₅)(Tp*)],^{6b} though the Class **A** carbido

complex [W₂(μ -C)(=NR)Cl₂(OSi^tBu₃)₄] (R = C₆H₃Me₂-2,6) arises from scission of a coordinated isonitrile (CNR).^{5d} Two approaches were successfully investigated involving either (i) ligand substitution processes commencing with **1** or alternatively (ii) oxidative addition reactions of **2** with a zerovalent platinum isonitrile precursor.

Combining **1** with an equivalent of an arylisonitrile in toluene results in phosphine substitution to provide [WPt(μ -C)Br(CNR)(PPh₃)(CO)₂(Tp*)] (R = C₆H₃Me₂-2,6 **3a**, C₆H₂Me₃-2,4,6 **3b**, Scheme 2). The Class **B** description remains appropriate with the *d*⁸ square-planar geometry at platinum being retained, as confirmed crystallographically for both **3a** (Figure 1) and **3b** (See ESI). As observed for **1**,^{6l} in solution both **3a** and **3b** exist as two rotamers with respect to the W–C–Pt–Br axis (ratio *ca* 4:1) that do not interconvert on the ³¹P NMR timescale (25 °C, 162 MHz). The formation of **3a** is accompanied by a shift of the carbido ¹³C resonance to lower frequency (δ_c = 308.4) compared with **1** (δ_c = 318.1) while the ¹⁹⁵Pt resonance (*d*, δ_{Pt} = –3761, ¹*J*_{Pt} = 3466



Scheme 2. Class **B** μ -carbido complexes bearing isonitrile ligands *en route* to imidoketenylidenes. *Reagents and conditions:* (i) CNR, toluene; (ii) CNR, toluene, Δ ; (iii) CNR, NaPF₆/NaBPh₄, MeOH/CH₂Cl₂; (iv) PPh₃, NaPF₆/NaBPh₄, MeOH/CH₂Cl₂.

Hz) remains in a similar region to those for the two rotamers of **1** (*t*, δ_{Pt} = –3812, –3718). Heating **1** with excess CNR C₆H₂Me₃ in refluxing toluene results in further phosphine substitution to afford *trans*-[WPt(μ -C)(CNC₆H₂Me₃)₂(CO)₂(Tp*)] (**4b**) which is also the product of the oxidative-addition reaction of **2** with *triangulo*-[Pt₃(CNC₆H₂Me₃-2,4,6)₆]. For **3a**, the triple W1–C1 [1.843(4) Å] and single C1–Pt1 [1.940(4) Å] bond lengths fall within ranges established for octahedral tungsten⁹ and square-planar platinum centres, respectively.¹⁰ The W1–C1–Pt1 spine is somewhat bent [168.4(3)°] so as to accommodate the phosphine ligand within a cleft provided by two pyrazolyl groups. The carbido ligand exerts a significant *trans* influence on

the bromide ligand [2.5248(7) Å], the implications of which will become apparent.

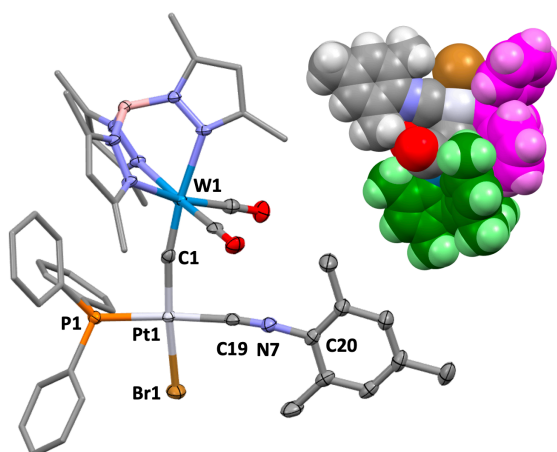


Figure 1. Molecular structure of **3a** in a crystal of **3a**.CH₂Cl₂. (50% displacement ellipsoids, pyrazolyl and phenyl rings simplified, solvent and hydrogens omitted for clarity). Selected bond lengths (Å) and angles (°): W1–C1 1.843(4), C1–Pt1 1.940(4), W1–C1–Pt1 168.4(3), Pt1–Br1 2.5248(7), Pt1–P1 2.309(1), Pt1–C19 1.996(6), C19–N7 1.145(8), C19–N7–C20 172.6(5). Inset = space-filling depiction of PPh₃ (magenta) and Tp* (green) ligand interdigitation.

During the formation of **3a** in toluene, no further reaction occurs between **3a** and the equivalent of liberated phosphine. Remarkably, however, when **3a** is combined with PPh₃ in a polar solvent combination (MeOH:CH₂Cl₂::1:10) a colour change to deep purple ensues which we initially, attributed to the formation of the salt [WPt(μ-C)(CNC₆H₃Me₂-2,6)(PPh₃)₂(CO)₂(Tp*)]Br given that the salt [WPt(μ-C)(terpy)(CO)₂(Tp*)]PF₆ (terpy = 2,2';6'2''-terpyridine) is also intense purple in colour.^{6j,l} While many of the spectroscopic data (ESI-MS, IR, ¹H NMR) were consistent with this formulation, two were conspicuously not. Firstly, Pt–Br ionization should have been attended by an increase in the infrared frequency of the isonitrile ν_{CN} absorption but counter-intuitively this dropped from 2196 cm⁻¹ in **3a** to 2104 cm⁻¹. More disconcerting was the failure to discern any resonance in the ¹³C{¹H} NMR spectrum in the region (δ_C = 300–500) characteristic of μ-carbido ligands. Instead, a resonance was observed at δ_C = 226.5 showing coupling to ¹⁸³W (158 Hz), ¹⁹⁵Pt (48 Hz) nuclei and one ³¹P (6 Hz) nucleus, while the ³¹P{¹H} NMR spectrum indicated two chemically inequivalent phosphine environments. These data were more consistent with coupling of the carbido and isonitrile ligands having occurred and the identity of the cation which features a bridging iminoketenylidene ligand was confirmed by crystallographic analyses of the salts [W(CCNC₆H₃Me₂-2,6)(CO)₂(PPh₃)₂][BPh₄] (**[5a]**), X = BPh₄, PF₆ Figure 2).

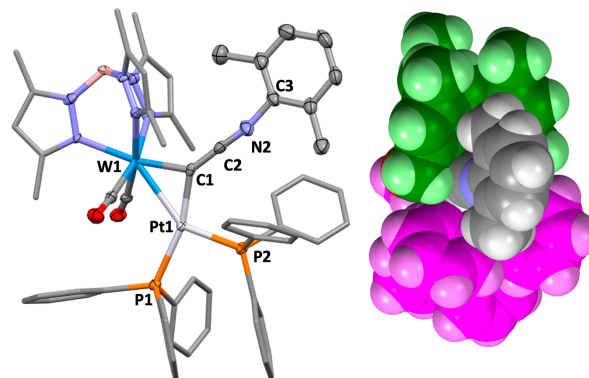


Figure 2: Molecular structure of **[5a]⁺** in a crystal of **[5a]**.PF₆.CHCl₃ (50% displacement ellipsoids, pyrazolyl and phenyl rings simplified. Solvent, hydrogens and PF₆ anion omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.997(5), Pt1–C1 1.996(5), C1–C2 1.350(8), C2–N1 1.162(8), N1–C3 1.393(8), W1–C1–Pt1 88.5(2), C1–Pt1–W1 45.8(1), Pt1–W1–C1 45.8(1), C3–N1–C2 163.8(6). Inset: space-filling representation (Tp* green, PPh₃ magenta)

The only notable difference between the structures of the **[5a]⁺** cations in the two salts is that for **[5a]PF₆** the xylyl and W1/C1/Pt1/P1/P2 mean planes are nearer to co-planar (18.1°) while for **[5a]BPh₄** this angle increases to 34.6° so as to accommodate intermolecular interactions with the bulbous counter-anion. Further discussion will involve **[5a]PF₆** for which the most notable observation is that the C1–C2–N1–C3 spine is close to linear with the largest deviation being a modest bend at N2 [163.8(6)°]. The question as to whether the iminoketenylidene ligand would be inclined to bend at nitrogen, thereby developing lone-pair character at nitrogen (cf. imines and hypothetical singlet CCNPh) is moot here because the aryl group lies in a valley straddled by two pyrazolyl and two phenyl groups. Molecular modelling (see ESI) indicates that more pronounced bending, either towards the PPh₃ or Tp* ligands would not actually be geometrically possible, a point to which we will return when considering the bonding from a computational standpoint (*vide infra*).

The W1–C1 bond length [1.997(5) Å] is considerably elongated relative to that of the precursor [1.843(4) Å], being comparable to those found for tungsten-platinum phosphoniocarbonyl-bridges (μ-CPR₃: 1.968–1.998Å^[11]), as is the corresponding Pt1–C1 distance. Bond lengths along the iminoketenylidene spine are best represented as cumulated double C=C [1.350(8) Å] and C=N [1.162(8) Å] bonds, ending with a single N–C [1.393(8) Å] bond to the aryl substituent.

Similar treatment of **3b** provided the isonitrile-iminoketenylidene salt [WPt(μ-CCNR)(CO)₂(CNR)(PPh₃)]PF₆ (**[5b]**)PF₆, R = C₆H₂Me₃-2,4,6), the yield of which was optimised by addition of extraneous isonitrile, or alternatively by treating **4b** with PPh₃ in CH₂Cl₂/MeOH mixtures. The doublet resonance observed at δ_C = 217.9 shows identical ²J_{PC} coupling (6 Hz) to that for **[5a]⁺** indicating that the phosphine is *pseudo-trans* to the iminoketenylidene μ-C carbon (Scheme 2). Two intense infrared absorptions are observed at 2115 and 2156 cm⁻¹ however computational analysis including a vibrational frequency calculation for the model complex [WPt(μ-CCNMe)(CNMe)(PMe₃)(CO)₂(Tp)]⁺ (*vide infra*) indicates that the

platinum-bound Pt-CN and iminoketenylidene C=C=N oscillators are strongly coupled rather than independent. Infrared data for the *iminoketenyl* complexes $[\text{Mn}\{\text{C}(\text{CNR})\text{R}'\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$ (R = Me, Cy, ^tBu; R' = Me, Ph)^{4f} include intense absorptions in the range 2212–2250 cm^{-1} .

Complexes with μ_2 -ketenylidene ligands are limited to the linear uranium complex $[\text{Cp}'_3\text{U-OCC-UCp}'_3]$ (Cp' = $\eta\text{-C}_5\text{H}_4\text{SiMe}_3$)^{12a} and the symmetrically bridging complexes $[\text{Zr}_3(\mu\text{-CCO})(\mu_3\text{-O})(\text{O}_2\text{CN}^+\text{Pr}_2)_6(\eta\text{-C}_5\text{H}_5)_2]$ ^{12b} and $[\text{OsRhH}(\mu\text{-CCO})(\text{CO})_3(\text{dppm})_2]$,^{12c} while a single example of a thioketenylidene complex $[\text{Mo}_2(\mu\text{-CCS})(\text{CO})_4(\text{Tp}^*)_2]$ has been reported.¹³ The CCO and CCS molecules have conical ($C_{\infty v}$) symmetry with doubly degenerate π and π^* orbital pairs, hence their triplet configuration. The frontier orbitals of hypothetical singlet CCNMe (**6_sMe**), singlet CNPh (**6_sPh**) and triplet (**6_tPh**) are detailed in the ESI[†],^{14,15}. For **6_tPh** the CCNC spine is near linear while **6_sPh** is bent (121.1°) at nitrogen, lying *ca* 10 kcal mol^{-1} (RI-MP2/cc-pVT ζ) below **6_sPh**. The geometry of the CCNR ligands in **[5]**⁺ most closely approximate that of **6_tPh**, although we contend that the near linear CCNC arrangement is a geometric corollary enforced by inter-ligand steric effects. The frontier orbitals of **6_sPh** are not dissimilar in topology to those of **6_tPh** and include an occupied orbital of σ -symmetry (soHOMO-4) in addition to singly occupied (soHOMO, SOMO) and unoccupied (LUMO, LUMO+1) orbitals of π -symmetry, thereby comprising a manifold well-disposed to synergic bonding with one or more metals. As a ligand it is therefore a monofacial^{4g} π -acceptor but might in principle serve as a bifacial π -donor towards metals with lower d-occupancies than employed here ($d^6\text{-W}$, $d^8\text{-Pt}$).

The fragment frontier orbitals presented by **6_tPh** are most relevant to the iminoketenylidene geometry found in **[5a]**⁺. We make this assumption based on (i) molecular modelling (*vide supra* and ESI[†]) and (ii) The geometry optimisation ($\omega\text{B97X-D}/6\text{-31G}^*/\text{LANL2D}\zeta(\text{W,Pt})$) for the sterically pruned model complexes $[\text{WPt}(\mu\text{-CCNMe})(\text{CO})_2(\text{L})(\text{PMe}_3)\text{Tp}]^+$ which have C–N–C angles of 161.0° (L = PMe_3 **7MeP**) and 167.2° (L = CNMe **7MeC**, see ESI[†]). The frontier orbitals of the model complex $[\text{WPt}(\mu\text{-CCNC}_6\text{H}_3\text{Me}_3)(\text{PMe}_3)_2(\text{Tp})]^+$ (**7MesP**) are shown in Figure 3. Those for $[\text{W}(\mu\text{-CCNMe})(\text{CNMe})(\text{PMe}_3)(\text{CO})_2(\text{Tp})]^+$ (**7MeC**, a model for **[5b]**⁺) are generally similar (ESI[†]).

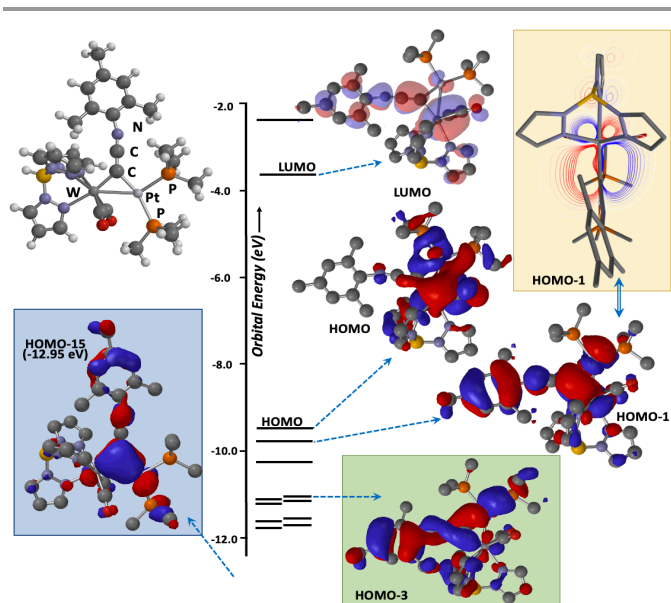


Figure 3. Frontier orbitals of interest and optimised geometry (DFT: $\omega\text{B97X-D}/6\text{-31G}^*/\text{LANL2D}\zeta(\text{W,Pt})$) of $[\text{WPt}(\mu\text{-CCNC}_6\text{H}_3\text{Me}_3)(\text{PMe}_3)_2(\text{Tp})]^+$ (**7MesP**, H-atoms omitted). Insets = (i) Metallacyclopropene fully π -bonding orbital (HOMO-15, blue); (ii) Helical orbital (HOMO-3, green) and (iii) Contours of HOMO-1 along W–C vector orthogonal to PtWC plane emphasising W–C π -bonding (beige).

The HOMO is primarily associated with W–CO π -retrodonation, while the HOMO-1 corresponds to the W–C π -bonding to the iminoketenylidene (Inset, Figure 3). This substantiates the canonical description of a dimetallacyclopropene core that might be deconstructed as a ‘PtL₂’ adduct of the hypothetical iminoketenylidene complex $[\text{W}(\text{CCNR})(\text{CO})_2(\text{Tp}^*)]^+$, thereby drawing analogy with addition of zerovalent group 10 metal reagents across the WC bond of phosphonocarbynes.^{11,16} This view is consistent with the W–C and Pt–C bond lengths measured for **[5a]**⁺ [1.997(5), 1.996(5) Å] and calculated for **7MesP** (1.9745, 2.000 Å) and derived Löwdin bond orders (W–C1 1.42; Pt–C 0.95, W–Pt 0.76). Deeper within the orbital manifold, however, the HOMO-15 involves fully π -bonding character between tungsten, carbon and platinum. The HOMO-3 displays an intriguing topology wherein overlap of the d-orbitals of both metal termini extends up the imidoketenylidene spine into the aromatic xylyl system in a helical manner so as to maintain a continuous albeit limited overlap as the nodal surface propagates helically. This is a feature of the molecular orbitals of $[n]$ cumulenes described by Hoffmann as Möbius co-arcate systems,¹⁷ wherein remote orthogonal orbitals of π -symmetry mix through an extended helically conjugated system. The LUMO is associated with the CCN π -system and, in an antibonding manner, with one tungsten $d\pi$ orbital, *i.e.*, were nucleophilic attack to occur, this would lead in the first instance to a μ -iminoketenyl ligand¹⁸ with reduced W–C bond order.

The most striking feature of the iminoketenylidene complexes is their intense purple colour (CH_2Cl_2 absorption: $\lambda_{\text{max}}/\text{nm}[\epsilon/\text{M}^{-1}\text{cm}^{-1}]$ **[5a]**⁺: 535[6900]; **[5b]**⁺: 550[6800]). From Figure 3, HOMO/HOMO-2 are W–CO π -bonding while HOMO-1 corresponds to the W=C π -bond. While the LUMO and LUMO+1 have some W–C π -antibonding character they are substantially

associated with π -bonding in the C=C=N unit, i.e., a degree of charge transfer ($d_{xy}/\pi_{WC} \rightarrow \pi^*_{WC}/\pi_{CCN}$) is associated with the electronic transitions. On the basis of TD-DFT analysis of **6MesP** (ESI[†]), predicted bands at 452 and 512 nm correspond primarily to HOMO-1/HOMO-2 \rightarrow LUMO transitions.

In conclusion, previously unknown iminoketenylidene ligands have been shown to be viable and able to bridge (hetero)bimetallic systems. The coupling of carbido and isonitrile ligands, whilst unprecedented, recalls the coupling of putative cluster-bound carbido centres with CO ligands.

Acknowledgements

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