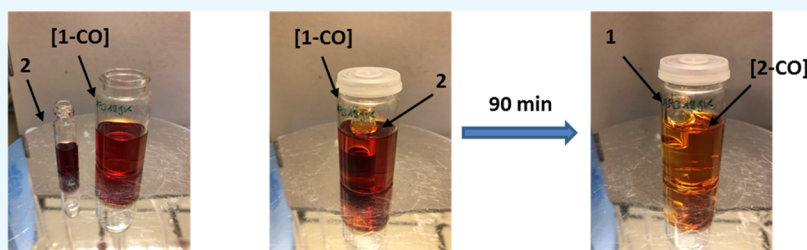


Controlled Release of Carbon Monoxide from a Pseudo Electron-Deficient Organometallic Complex

Anaïs Pitto-Barry¹ and Nicolas P. E. Barry^{1*}

School of Chemistry and Biosciences, University of Bradford, Bradford BD7 1DP, U.K.

Supporting Information



ABSTRACT: A 16-electron iridium organometallic is reacted with carbon monoxide to form an 18-electron CO-adduct. This CO-adduct is stable for weeks in the solid state, but quickly reverts to its parent 16-e complex in tetrahydrofuran solution, releasing CO_(g). Using a simple methodology, we show that this gas can subsequently be used to perform a carbonylation reaction on another molecule.

INTRODUCTION

Carbonylation reactions are used for the large-scale production of aldehydes (via hydroformylation) and carboxylic acids (e.g., acetic acid via the Cativa process).¹ In such large-scale industrial processes, the utilization of carbon monoxide cylinders is unreplaceable because of their cost-effectiveness as well as for practical reasons (e.g., transport and storage of large quantities of carbon monoxide). However, carbon monoxide is a poisonous gas that has no smell or taste (so-called “silent killer”).² The toxicity of carbon monoxide makes the utilization of CO cylinders difficult for small-scale reactions in laboratories, and the purchase and handling of such cylinders are strictly regulated. Therefore, there has been a long and significant academic and industrial interest in the development of materials capable of reversibly capturing and releasing CO.^{3–6} A number of CO surrogates which can avoid the utilization of CO gas cylinders have been developed by Skrydstrup and co-workers^{7–13} and others.^{14–18} However, this is still an extremely challenging quest owing to the difficulty to desorb the ligand from existing carbon monoxide-containing materials,^{19–23} without irreversibly damaging them.²⁴

We have recently reported a simple strategy for the fabrication of electron-deficient organometallics-containing gels that allow the nearly quantitative capture of a known amount of carbon monoxide.²⁵ Importantly, we demonstrated the straightforward release of CO from the metallated gels and the recovery of the original materials at ambient temperature and ambient pressure by simply dipping the CO-containing gels in a tetrahydrofuran (THF) solution. However, we observed that after some minutes in THF (and thus after several recycling steps), the structures of the gels tend to loss

their integrity, which limits the reusability of these materials and some of their potential applications.

Here, we report a new strategy for the controlled release of known quantities of carbon monoxide, without formulating organometallic complexes into gels. The electron-deficient organometallic complex [Ir(η^5 -pentamethylcyclopentadiene)-(benzene-1,2-dithiolato)] (**1**; Scheme 1) is shown to exhibit a peculiar reactivity with the σ -donor, π -acceptor carbon monoxide ligand, leading to the formation of the 18-electron adduct [Ir(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)(CO)] ([**1-CO**]). The ability of complex [**1-CO**] to release carbon monoxide under mild and controlled conditions is studied, and its application as a source of CO for carbonylation reactions is investigated.

RESULTS AND DISCUSSION

The reactivity in solution of [Ir(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (**1**) with CO was first investigated in dichloromethane solution (Figure 1a). Iridium complex **1** readily forms the 18-electron adduct [Ir(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)(CO)] ([**1-CO**]) in solution when CO_(g) is bubbled into the solution. UV–visible absorption spectroscopy suggests the formation of the CO 18-e adducts (Figure 1b), with the dramatic decrease of the absorption band observed at 440 nm (associated to ligand-to-metal charge-transfer transitions that are commonly observed in 16-electron complexes²⁶) which is in accordance with the formation of 18-e species for this metal

Received: August 24, 2018

Accepted: October 30, 2018

Published: November 16, 2018

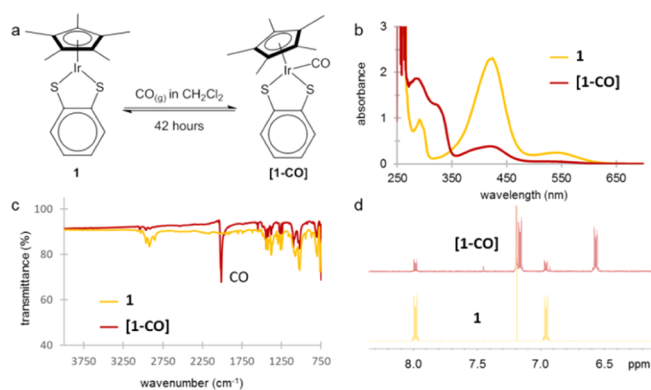


Figure 1. Synthesis (a) and UV–visible (10^{-4} M, CH_2Cl_2 , 298 K, b) IR (as powders, c) and ^1H NMR (CDCl_3 , 1 mM, 298 K, d) spectra of complexes **1** and **[1-CO]**.

complex.²⁷ The infrared spectroscopy spectra before and after CO exposure show the presence of the characteristic CO band at 1900 cm^{-1} after CO exposure (Figure 1c). ^1H NMR spectroscopy confirms the formation of the CO adduct **[1-CO]**, although the reaction is not complete with a conversion of ca. 80% (Figures 1d and S1). A time-dependent ^1H NMR study (1 mM, CDCl_3 , 298 K) of **[1-CO]** shows the decoordination of the CO ligand over time and the return to the parent complex **1** after 40 h (Figure S2). The molar percentages of **[1-CO]** in CDCl_3 solution during the release of CO from **[1-CO]** are presented in Table S1. Slow evaporation leads to the isolation of **[1-CO]** solid. Importantly, the CO spectroscopic signature in the **[1-CO]** solid is still observed after storage of the powder at ambient temperature, in an opened vial, for 1 h and for 4 weeks (Figure S3). Interestingly, the formation of **[1-CO]** can also be performed by exposing complex **1** as a solid to an atmosphere (1 atm) of CO, leading to a gas–solid reaction.

In THF solution, complex **[1-CO]** also readily reverses to the parent complex **1**, but after only a few minutes in solution (Figure 2). The decoordination of the carbon monoxide ligand

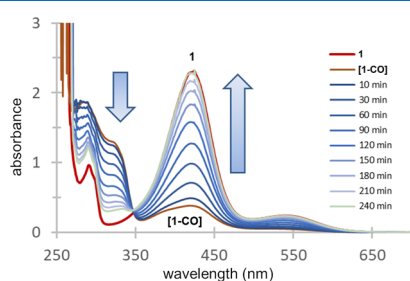


Figure 2. Time-dependent ^1H NMR spectra (1 mM, deuterated THF, 298 K) of **[1-CO]** showing the CO decoordination and the return to the parent complex **1**.

is faster in THF than in dichloromethane, which we hypothesize is due to the lower relative polarity of THF (0.207) compared to that of dichloromethane (0.309) or chloroform (0.272). This is in accordance with our previous report in which we found a direct correlation between the polarity of the solvents and the ability of pseudo electron-deficient organometallics to release CO when immersed in them.²⁵

The carbon monoxide decoordination in THF solution was investigated by UV–visible spectroscopy. From the time-

dependent UV–visible spectra shown in Figure 2, the decoordination constant K between complex **1** and the CO ligand was calculated as being $1.1 \pm 0.3 \times 10^3\text{ M}^{-1}$, using the nonlinear Thordarson Fitting Program.²⁸ The experimental Gibbs free energy (ΔG°) was obtained from the Gibbs equation using the calculated value of K and found to be $-4.1 \pm 0.4\text{ kcal}\cdot\text{mol}^{-1}$. The ^1H NMR spectra of **[1-CO]** in deuterated THF over time were also recorded. After 4 h (longer than in the UV–vis cuvette because of the narrowness and limited air exchange within the NMR tube), the decoordination of CO is half complete (Figure S4). The molar percentages of **[1-CO]** in deuterated-THF solution during the release of CO from **[1-CO]** are presented in Table S2.

It should be noted that the decoordination of the CO ligand in THF is much faster for complex **1** than for its carborane analogue (previously reported as one week for complete decoordination).²⁵ This is consistent with the studies in solution for both sets of complexes (carborane-containing versus benzene-containing).²⁹ Indeed, in the case of complex **1**, one of the sulfur atoms in the MS_2C_2 chelate ring acts as a three-electron donor to the metal atom and the other acts only as a one-electron donor.²⁹ This gives the metal the favored 18-electron configuration and makes it unreactive toward bases such as pyridine derivatives, but slightly reactive toward σ -donor and π -acceptor ligands, such as carbon monoxide. Thus, the actual structure of complex **1** is a resonance hybrid of the two canonical structures with the sulfur atoms in the two states, which leads to a pseudo 16-electron configuration. The carborane-containing analogue of **1** has an unsaturated 16-electron configuration (because of the bulkiness and electron-deficiency of the carborane ligand), making it more prone to reaction with both σ -donor and σ -donor and π -acceptor ligands.

The possibility of using the controlled release of CO by **[1-CO]** in THF as a source of carbon monoxide to perform a chemical reaction was then investigated. We attempted to transfer the CO ligand from **[1-CO]** to the metal center of the 16-electron organometallic complex $[\text{Os}(\eta^6\text{-}p\text{-cym})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})]$ (**2**) to form $[\text{Os}(\eta^6\text{-}p\text{-cym})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})(\text{CO})]$ (**[2-CO]**).

To do so, a methodology based on the “small-vial-inside-larger-vial” setup was used (Figure 3): first, 16 mol equiv of complex **1** (see the Supporting Information for the experimental procedure) was dissolved in THF in a large vial. CO was bubbled in the solution for a few minutes, until a change of color from deep red to red-orange was observed. The CO needle was removed and the vial was left open for 2 min to allow residual $\text{CO}_{(\text{g})}$ to be dispersed in the atmosphere. Second, 1 mol equiv of complex **2** was dissolved in CDCl_3 (1 mL) in a small vial equipped with a stirrer bar. This small vial was introduced in the larger vial that was then closed with a standard plastic cap. The solution in the small vial was stirred at 500 rpm. After 90 min, the solution in the bigger vial was observed to be less intense in color. The small vial was removed, and its content was immediately analyzed by ^1H NMR spectroscopy.

A color change from dark red (corresponding to complex **2** in CDCl_3) to yellow (corresponding to **[2-CO]** in CDCl_3) was observed. ^1H NMR spectroscopy (Figure 3) and infrared spectroscopy (Figure 4) demonstrate the complete formation of the Os complex **[2-CO]**.

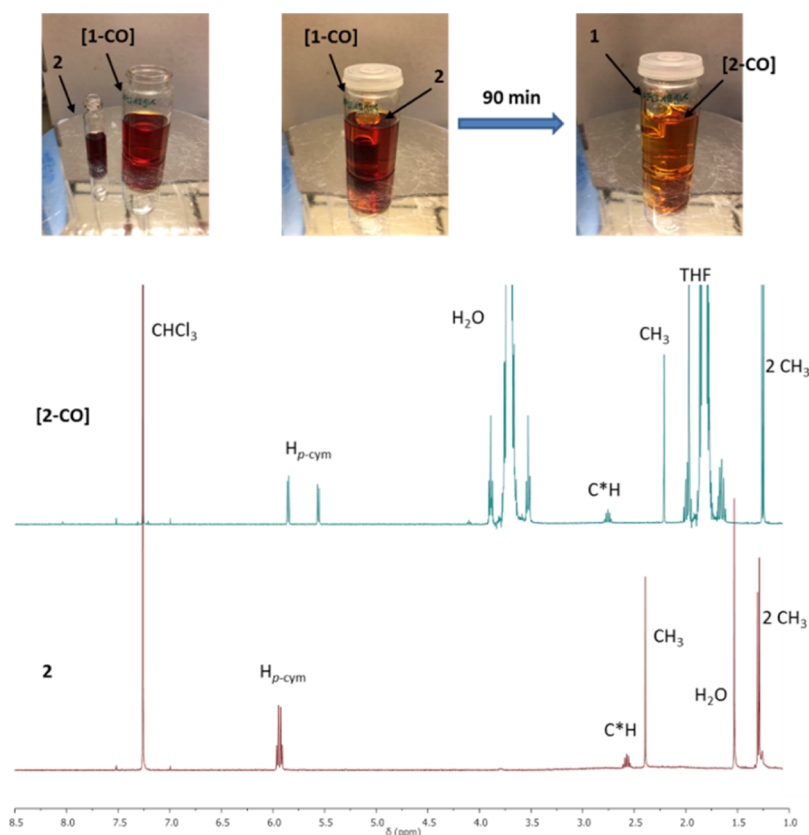


Figure 3. Top: Principle and experimental prototype for the “small-vial-inside-larger-vial” setup. Bottom: ¹H NMR spectra of complexes **2** and **[2-CO]** (1 mM, CDCl₃, 298 K). **[2-CO]** is obtained by carbonylation reaction between **2** in CDCl₃ located in a small vial and CO that was released from the **[1-CO]** solution in THF in the larger vial.

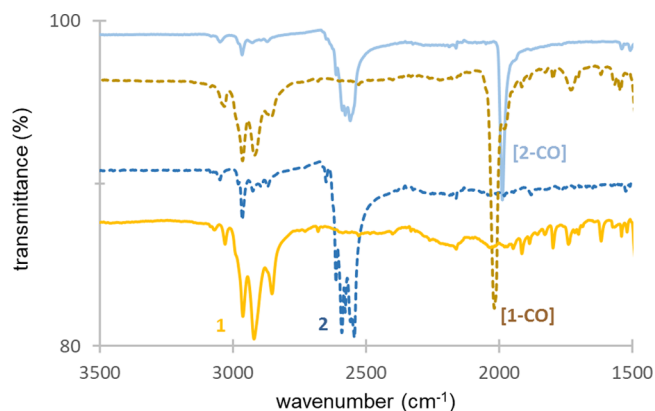


Figure 4. Infrared spectroscopy spectra of complexes **[1-CO]** and **2** before reaction and complexes **[2-CO]** and **1** after reaction.

To validate our hypothesis that Ir complex **[1-CO]** can be used as a substitute (for small-scale reactions) for gas cylinders as a safer way for the transport, storage, and handling of carbon monoxide, the following control experiment was carried out: the CO ligand exchange does not occur when the 18-e Ir complex **[1-CO]** and the 16-e Os complex **2** are mixed together in THF solution, probably because the CO escapes the THF solution too quickly.

CONCLUSIONS

Our results show that the iridium complex $[\text{Ir}(\eta^5\text{-pentamethylcyclopentadiene})(\text{benzene-1,2-dithiolato})]$ (**1**) can be functionalized with CO to form the CO-adduct **[1-**

CO], either in dichloromethane solution or in the solid state. In the solid form, **[1-CO]** is stable over a long period (weeks), allowing its facile storage and transport. The CO can be released, when required, by solubilizing **[1-CO]** in a vial. Using the hanging basket methodology, it is possible to carbonylate another metal complex by using a simple “vial-inside-vial” setup. This proof-of-concept study demonstrates that the controlled release of CO from the solution has the potential to generate small quantities of CO for small-scale reactions. Future work will involve control of the rate of release of CO from the complex in solution via design of ligands that will either slow or accelerate the release of CO. Ruthenium, osmium, and rhodium analogues of the Ir compound will be synthesized in order to optimize the system. The application of our methodology to the carbonylation of organic molecules will also be investigated. Owing to the toxicity and dangers associated with pressurized CO gas cylinders, we anticipate that our methodology has potential for safer transport and storage of small, known, quantities of carbon monoxide.

MATERIALS AND METHODS

Materials. The preparations of the complexes $[\text{Ir}(\eta^5\text{-pentamethylcyclopentadiene})(\text{benzene-1,2-dithiolato})]$ (**1**) and $[\text{Os}(\eta^6\text{-}p\text{-cym})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})]$ (**2**) were based on previous reports.^{29,30} Anhydrous quality THF, diethyl ether, and methanol were purchased from Sigma-Aldrich. *o*-Carborane was purchased from Katchem and used as received.

CO is a Toxic Gas. All experiments involving the use of CO were conducted in a fumehood, with researchers having portable CO detectors with them at all times.

Instrumentation. UV–visible absorption spectra were recorded using a Varian CARY 50 Bio UV–visible spectrophotometer at 298 K using 1 cm path length quartz cuvettes. All infra-red spectra were recorded on a Bruker Alpha Platinum ATR. All NMR spectra were recorded on a 400 MHz Bruker Spectrospin spectrometer using deuterated solvents. Chemical shifts are reported as δ in parts per million using the residual protonated solvent as internal standard.³¹

Synthesis and Characterization. Coordination of 1 with CO in Solution. Complex 1 was dissolved in the solvent of choice. A needle connected to the CO cylinder by some Tygon tubing was then purged by flushing some CO through. After 2 min of purge, the needle was introduced into the solution and CO(g) was bubbled in the solution for 3 min. The solutions were then analyzed. For ¹H NMR studies, complex 1 (0.9 mg, 2 μ mol) was dissolved in 2 mL of CDCl₃ or deuterated THF to obtain a 1 mmol/L concentration. For UV–visible studies, complex 1 (1.1 mg, 2.4 μ mol) was dissolved in 23.52 mL of solvent (THF or CH₂Cl₂) to obtain a 10⁻⁴ mol/L concentration.

Coordination of 1 with CO in the Solid State. Complex 1 (2–3 mg) was introduced in a vial (15 mL). The vial was closed with a septum. A needle connected to the vacuum was used to create a light vacuum in the vial (the septum slightly shrunk). The CO tubing and the end needle were purged by flushing some CO through for 2 min. The end needle was connected to the vial, and CO(g) was introduced into the vial. At the same time, an exit needle was connected to the vial to avoid any CO excessive pressure. After 5 min of CO flow, the two needles were removed, and the vial was left open close to 1 h before any analyses were conducted.

Carbonylation Reaction between [1-CO] and 2 with the Vial-In-A-Vial Strategy. Complex 1 (15.9 mg, 34.0 μ mol) was dissolved in THF (9 mL) in a 20 mL scintillation vial. CO was bubbled in the solution for 3 min. A change of color from deep red to red-orange was observed. The CO needle was removed, and the vial was left open for 2 min to allow CO(g) to be dispersed in the air.

Complex 2 (1 mg, 1.9 μ mol) was dissolved in CDCl₃ (1 mL) in a 2 mL high-performance liquid chromatography vial equipped with a stirrer bar. This small vial was introduced in the 20 mL scintillation vial that was then closed with a standard plastic cap. The solution in the small vial was stirred at 500 rpm. After 90 min, the solution in the big vial was observed to be less intense in color. The small vial was removed and its content was immediately analyzed by ¹H NMR spectroscopy.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02154.

Supporting figures and tables (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: N.Barry@bradford.ac.uk (N.P.E.B.).

ORCID

Anaïs Pitto-Barry: 0000-0001-5100-0922

Nicolas P. E. Barry: 0000-0002-0388-6295

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the Royal Society (University Research Fellowship no. UF150295 to N.P.E.B.) and by the Academy of Medical Sciences/the Wellcome Trust/the Government Department of Business, Energy and Industrial Strategy/the British Heart Foundation Springboard Award [SBF003\1170]. We also thank Maria Azmanova for technical assistance in the laboratory.

■ REFERENCES

- (1) De Risi, C.; Pollini, G. P.; Zanirato, V. Recent Developments in General Methodologies for the Synthesis of α -Ketoamides. *Chem. Rev.* **2016**, *116*, 3241–3305.
- (2) Carrette, L.; Friedrich, K. A.; Stimming, U. Fuel Cells: Principles, Types, Fuels, and Applications. *ChemPhysChem* **2000**, *1*, 162–193.
- (3) Kustov, L. M.; Kazanskii, V. B.; Beran, S.; Kubelkova, L.; Jiru, P. Adsorption of carbon monoxide on ZSM-5 zeolites: infrared spectroscopic study and quantum-chemical calculations. *J. Phys. Chem.* **1987**, *91*, 5247–5251.
- (4) Sahraie, N. R.; Kramm, U. I.; Steinberg, J.; Zhang, Y.; Thomas, A.; Reier, T.; Paraknowitsch, J.-P.; Strasser, P. Quantifying the density and utilization of active sites in non-precious metal oxygen electroreduction catalysts. *Nat. Commun.* **2015**, *6*, 9618.
- (5) Tarach, K.; Góra-Marek, K.; Chrzan, M.; Walas, S. Quantification of Silver Sites in Zeolites: Carbon Monoxide Sorption Monitored by IR Spectroscopy. *J. Phys. Chem. C* **2014**, *118*, 23751–23760.
- (6) Kim, W. B.; Voitl, T.; Rodriguez-Rivera, G. J.; Dumesic, J. A. Powering Fuel Cells with CO via Aqueous Polyoxometalates and Gold Catalysts. *Science* **2004**, *305*, 1280–1283.
- (7) Makarov, I. S.; Kuwahara, T.; Jusseau, X.; Ryu, I.; Lindhardt, A. T.; Skrydstrup, T. Palladium-Catalyzed Carbonylative Couplings of Vinylogous Enolates: Application to Statin Structures. *J. Am. Chem. Soc.* **2015**, *137*, 14043–14046.
- (8) Neumann, K. T.; Lindhardt, A. T.; Bang-Andersen, B.; Skrydstrup, T. Access to 2-(Het)aryl and 2-Styryl Benzoxazoles via Palladium-Catalyzed Aminocarbonylation of Aryl and Vinyl Bromides. *Org. Lett.* **2015**, *17*, 2094–2097.
- (9) Lian, Z.; Yin, H.; Friis, S. D.; Skrydstrup, T. Pd-catalyzed carbonylative access to aroyl phosphonates from (hetero)aryl bromides. *Chem. Commun.* **2015**, *51*, 7831–7834.
- (10) Yin, H.; Kumke, J. J.; Domino, K.; Skrydstrup, T. Palladium Catalyzed Carbonylative Coupling of Alkyl Boron Reagents with Bromodifluoroacetamides. *ACS Catal.* **2018**, *8*, 3853–3858.
- (11) Friis, S. D.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. Silacarboxylic Acids as Efficient Carbon Monoxide Releasing Molecules: Synthesis and Application in Palladium-Catalyzed Carbonylation Reactions. *J. Am. Chem. Soc.* **2011**, *133*, 18114–18117.
- (12) Hermange, P.; Lindhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. Ex Situ Generation of Stoichiometric and Substoichiometric 12CO and 13CO and Its Efficient Incorporation in Palladium Catalyzed Aminocarbonylations. *J. Am. Chem. Soc.* **2011**, *133*, 6061–6071.
- (13) Friis, S. D.; Lindhardt, A. T.; Skrydstrup, T. The Development and Application of Two-Chamber Reactors and Carbon Monoxide Precursors for Safe Carbonylation Reactions. *Acc. Chem. Res.* **2016**, *49*, 594–605.
- (14) Li, X.-F.; Shi, L.-F.; Zhang, X.-G.; Zhang, X.-H. Pd-Catalyzed C(sp²)-H aminocarbonylation using the Langlois reagent as a carbonyl source. *Org. Biomol. Chem.* **2018**, *16*, 6438–6442.

(15) Wang, H.; Ying, J.; Lai, M.; Qi, X.; Peng, J.-B.; Wu, X.-F. Base-Promoted Carbonylative Cyclization of Propargylic Amines with Selenium under CO Gas-free Conditions. *Adv. Synth. Catal.* **2018**, *360*, 1693–1703.

(16) Ying, J.; Zhou, C.; Wu, X.-F. DBU-promoted carbonylative synthesis of 1,3-oxathiolan-2-ones from propargylic alcohols with TFBen as the CO source. *Org. Biomol. Chem.* **2018**, *16*, 1065–1067.

(17) Magné, V.; Lorton, C.; Marinetti, A.; Guinchard, X.; Voituriez, A. Short Enantioselective Total Synthesis of (–)-Rhazinilam Using a Gold(I)-Catalyzed Cyclization. *Org. Lett.* **2017**, *19*, 4794–4797.

(18) Norderman, P.; Odell, L. R.; Larhed, M. Aminocarbonylations Employing Mo(CO)₆ and a Bridged Two-Vial System: Allowing the Use of Nitro Group Substituted Aryl Iodides and Aryl Bromides. *J. Org. Chem.* **2012**, *77*, 11393–11398.

(19) Sato, H.; Kosaka, W.; Matsuda, R.; Hori, A.; Hijikata, Y.; Belosludov, R. V.; Sakaki, S.; Takata, M.; Kitagawa, S. Self-Accelerating CO Sorption in a Soft Nanoporous Crystal. *Science* **2014**, *343*, 167–170.

(20) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. Dioxygen-copper reactivity. Reversible binding of O₂ and CO to a phenoxo-bridged dicopper(I) complex. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679.

(21) Hudnall, T. W.; Bielawski, C. W. An N,N'-Diamidocarbene: Studies in C–H Insertion, Reversible Carbonylation, and Transition-Metal Coordination Chemistry. *J. Am. Chem. Soc.* **2009**, *131*, 16039–16041.

(22) Raeissi, S.; Florusse, L. J.; Peters, C. J. Purification of flue gas by ionic liquids: Carbon monoxide capture in [bmim][Tf₂N]. *AIChE J.* **2013**, *59*, 3886–3891.

(23) Tao, D.-J.; Chen, F.-F.; Tian, Z.-Q.; Huang, K.; Mahurin, S. M.; Jiang, D.-e.; Dai, S. Highly Efficient Carbon Monoxide Capture by Carbanion-Functionalized Ionic Liquids through C-Site Interactions. *Angew. Chem., Int. Ed.* **2017**, *56*, 6843–6847.

(24) Tsukada, S.; Sagawa, T.; Gunji, T. Carbon Monoxide Addition to Ruthenium–Dithiolene Complex and Polysiloxane Hybrid Film Formation. *Chem.—Asian J.* **2015**, *10*, 1881–1883.

(25) Pitto-Barry, A.; Lupan, A.; Ellingford, C.; Attia, A. A. A.; Barry, N. P. E. New Class of Hybrid Materials for Detection, Capture, and “On-Demand” Release of Carbon Monoxide. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13693–13701.

(26) Mashima, K.; Kaneyoshi, H.; Kaneko, S.-i.; Mikami, A.; Tani, K.; Nakamura, A. Chemistry of Coordinatively Unsaturated Bis-(thiolato)ruthenium(II) Complexes (η^6 -arene)Ru(SAr)₂ [SAr = 2,6-Dimethylbenzenethiolate, 2,4,6-Triisopropylbenzenethiolate; (SAr)₂ = 1,2-Benzenedithiolate; Arene = Benzene, p-Cymene, Hexamethylbenzene]. *Organometallics* **1997**, *16*, 1016–1025.

(27) Barry, N. P. E.; Deeth, R. J.; Clarkson, G. J.; Prokes, I.; Sadler, P. J. Thermochromic organometallic complexes: experimental and theoretical studies of 16- to 18-electron interconversions of adducts of arene Ru(II) carboranes with aromatic amine ligands. *Dalton Trans.* **2013**, *42*, 2580–2587.

(28) Thordarson, P. Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

(29) Pitto-Barry, A.; Lupan, A.; Zegke, M.; Swift, T.; Attia, A. A. A.; Lord, R. M.; Barry, N. P. E. Pseudo electron-deficient organometallics: limited reactivity towards electron-donating ligands. *Dalton Trans.* **2017**, *46*, 15676–15683.

(30) Pitto-Barry, A.; South, A.; Rodger, A.; Barry, N. P. E. The synthesis and unexpected solution chemistry of thermochromic carborane-containing osmium half-sandwich complexes. *Dalton Trans.* **2016**, *45*, 1763–1768.

(31) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.