Coordination Chemistry

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A Classical Silver Carbonyl Complex [{MeB[3-(Mes)pz]$_3$}Ag(CO)] and the Related Silver Ethylene Adduct [{MeB[3-(Mes)pz]$_3$}Ag(C_2H_4)]**

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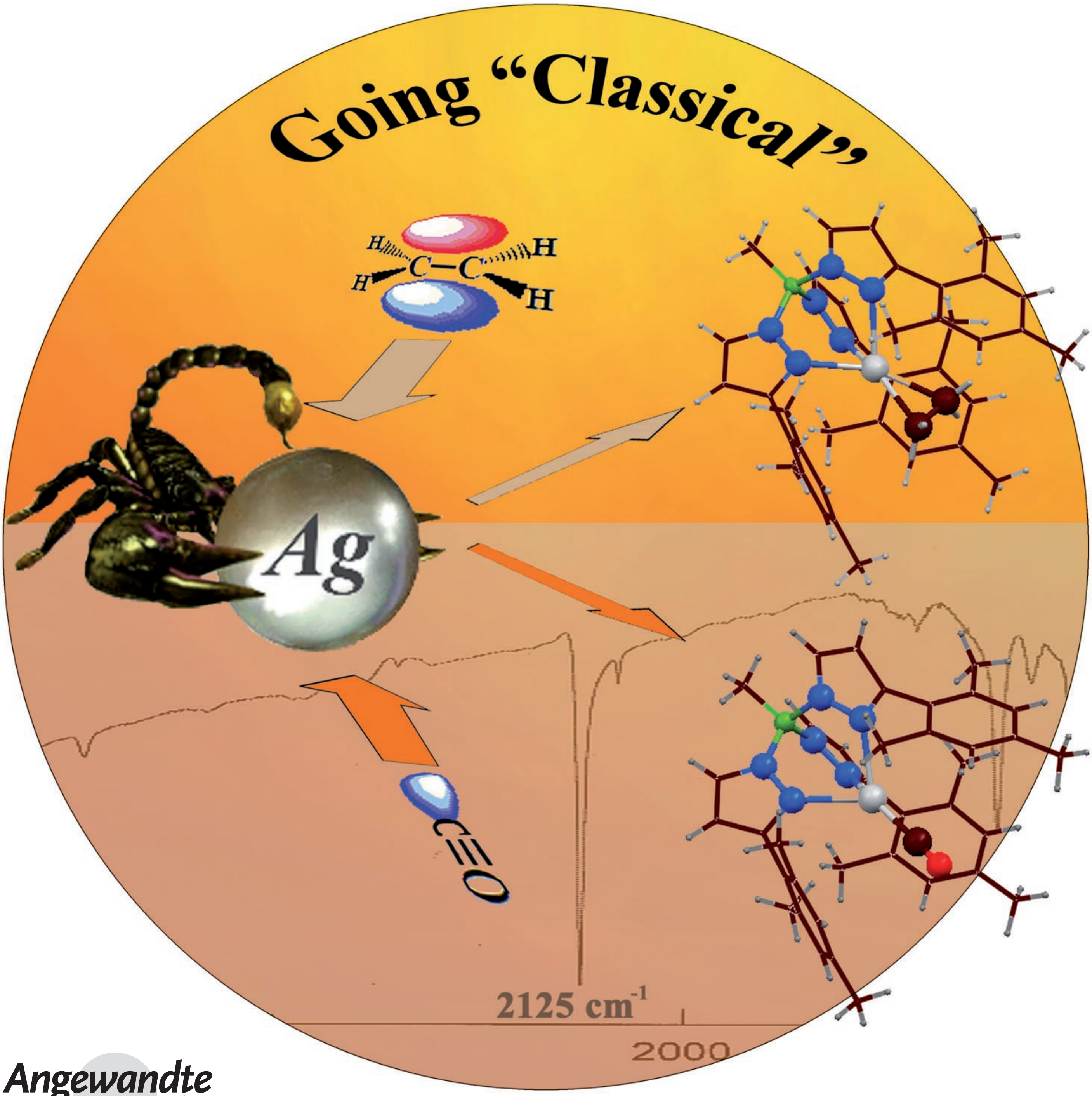

Angewandte Chemie

Silver complexes of small unsaturated molecules such as carbon monoxide and ethylene are of tremendous fundamental importance and practical value.[1–7] Yet, structurally characterized silver(I) complexes featuring CO and C_2H_4 ligands are rare.[3–12] The isolation of such thermally stable adducts is a very challenging task because silver(I) is a poor σ acceptor, a poor π donor, and in general forms extremely labile adducts with π-acidic ligands.[1,6] The light sensitivity of silver adducts, the oxidizing nature of silver, and the easy displacement of the coordinated CO and C_2H_4 ligands by many other weakly donating species (which includes common solvents) present further synthetic challenges. The entropic factors arising from "fixing" gases are also believed to play a detrimental role.[7]

Despite theses difficulties, a few Ag^I–CO and Ag^I–C_2H_4 complexes have been isolated and characterized structurally. They include $[Ag(CO)_2][B(OTeF_5)_4]$, $[Ag(CO)][B(OTeF_5)_4]$,[8,9] $[\{HB[3,5\text{-}(CF_3)_2pz]_3\}Ag(CO)]$,[10] $[\{MeB[3\text{-}(C_2F_5)pz]_3\}Ag(CO)]$,[3] $[\{HB[3,5\text{-}(CF_3)_2pz]_3\}Ag(C_2H_4)]$,[11] $[\{MeB[3\text{-}(C_2F_5)pz]_3\}Ag(C_2H_4)]$,[3] $[Ag(C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$,[7] and $[\{HC\{(CF_3)C[3,5\text{-}(CF_3)_2C_6H_3]N\}_2\}Ag(C_2H_4)]$ (pz = pyrazolate).[12] All these compounds contain weakly coordinating, highly fluorinated ligands. Furthermore, silver(I) carbonyl adducts described above exhibit stretching frequencies for ν_{CO} higher than that for free CO (2143 cm^{-1}), and range from 2204 cm^{-1} in $[Ag(CO)][B(OTeF_5)_4]$ to 2153 cm^{-1} in $[\{MeB[3\text{-}(C_2F_5)pz]_3\}Ag(CO)]$. These are classified as nonclassical metal carbonyl complexes.[5,13] Herein, we describe the synthesis and structural characterization of the first classical silver carbonyl complex, along with the related silver(I) ethylene adduct. We also demonstrate the successful use of a nonfluorinated, relatively electron-rich ligand in Ag^I–CO and Ag^I–C_2H_4 chemistry.

The complex $[\{MeB[3\text{-}(Mes)pz]_3\}Ag(C_2H_4)]$ (**1**, Figure 1) is obtained through a metathesis reaction between the thallium salt $[MeB\{[3\text{-}(Mes)pz]_3\}Tl]$[14] and CF_3SO_3Ag in CH_2Cl_2 under an ethylene atmosphere, and is a white powder with remarkable stability. The ^1H NMR spectroscopic data collected from a week-old sample stored at room temperature in a dark container showed no decomposition.

The X-ray analysis revealed that **1** crystallizes in the *R*3*c* space group with a threefold rotation axis containing the B and Ag atoms (Figure 2). The tris(pyrazolyl)borate ligand coordinates to the silver ion in a tripodal fashion with an Ag–N bond length of 2.3404(14) Å. The ethylene moiety is distributed equally over three positions inside the coordination pit of the tris(pyrazolyl)borate ligand and coordinates to silver in an η^2-fashion with a C=C bond length of 1.323(12) Å. The corresponding distance in $[\{MeB[3\text{-}(C_2F_5)pz]_3\}Ag(C_2H_4)]$ is not significantly different at 1.314(4) Å.[3]

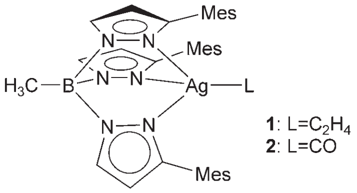

Figure 1. $[\{MeB[3\text{-}(Mes)pz]_3\}AgL]$ complexes (L = C_2H_4, CO). Mes = mesityl = 2,4,6-trimethylphenyl.

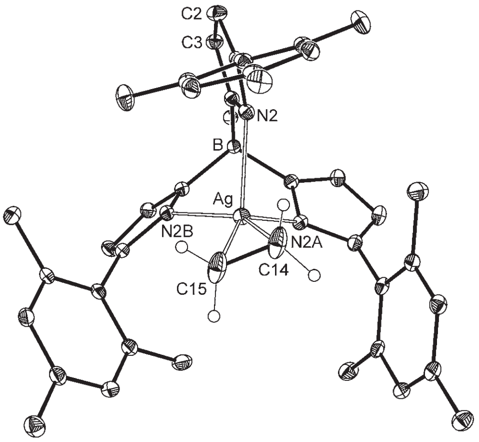

Figure 2. Molecular structure of **1**. All the hydrogen atoms, except those on ethylene moiety, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag-C14 2.27(3), Ag-C15 2.28(3), Ag-N2 2.3404(14), C14-C15 1.323(12), Ag···B 3.422; C14-Ag-C15 33.8(3). Thermal ellipsoids are set at the 35 % probability level.

The ^1H NMR signal corresponding to the ethylene group appears at $\delta = 3.42$ ppm in the spectrum recorded in $CDCl_3$, which is significantly upfield compared with the corresponding signal of free ethylene ($\delta = 5.40$ ppm).[15] The ^1H NMR spectra of related silver ethylene adducts with fluorinated ligands $[\{HB[3,5\text{-}(CF_3)_2pz]_3\}Ag(C_2H_4)]$[11] and $[\{MeB[3\text{-}(C_2F_5)pz]_3\}Ag(C_2H_4)]$[3] contain this signal at a relatively downfield region ($\delta = 5.56$ and 5.48 ppm, respectively). The upfield or downfield shifts of these signals resulting from a coordinated ethylene moiety have been previously correlated with an increase or decrease in the ability for $M \rightarrow C_2H_4$ π backbonding.[16] Although greater $Ag \rightarrow C_2H_4$ π backbonding is a possibility with **1**,[17] the relative magnitude of the shift is unusually high and indicates that some additional factors are contributing to the effect. One likely reason for a large upfield shift is the shielding caused by the ring-current effect of the three mesityl substituents that surround the ethylene unit. The ethylene moiety of $[HC\{(CF_3)C(3,5\text{-}(CF_3)_2C_6H_3)N\}_2][Ag(C_2H_4)]$[12] is somewhat flanked by aryl groups and the signal for the ethylene group is also shifted upfield ($\delta =$

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Supporting information for this article, including complete details of the synthesis, characterization, and additional X-ray structures, is available on the WWW under http://www.angewandte.org or from the author.

3.78 ppm in C_6D_6).[12] To further investigate this, we synthesized [{MeB[3-(Mes)pz]$_3$}Cu(C_2H_4)][18] and compared the ethylene signal in the ^{1}H NMR spectrum to that obtained for [{HB[3,5-(Me)$_2$pz]$_3$}-Cu(C_2H_4)] ($\delta = 2.61$ ppm and $\delta = 4.41$ ppm, respectively).[19] Although the latter has a relatively electron rich copper atom with a greater π-donor capability,[17] the upfield shift is relatively small compared with the signal for free ethylene ($\delta = 5.40$ ppm). These results are consistent with the possible contribution from ring-current effects, although further studies are required to justify this claim. The shifts in the ^{1}H NMR signals for the ethylene groups in the [{MeB[3-(Mes)pz]$_3$}M(C_2H_4)] adducts (M = Cu and Ag) are in agreement with the greater backbonding ability of copper(I) as compared to silver(I).[1,5,20]

Table 1: Selected structural and spectroscopic parameters for Au–CO compounds.[a]

	Compound	$\tilde{\nu}_{CO}$ [cm^{-1}]	Ag–C [Å]	Ag–N [Å][c]	C–O [Å]	Ref.
Nonclassical	[Ag(CO)][B($OTeF_5$)$_4$]	2204[b]	2.10(1)		1.077(16)	[22]
	[Ag(CO)$_2$][B($OTeF_5$)$_4$]	2198[b,c]	2.14(5)[c]		1.08(6)[c]	[22]
	[Ag(CO)][$OTeF_5$]	2189[b]				[22]
	[{HB[3,5-(CF_3)$_2$pz]$_3$}Ag(CO)]	2178[b]	2.037(5)	2.328(4)	1.116(7)	[10]
	[{HC[3-(*t*Bu)pz]$_3$}Ag(CO)]SO_3CF_3	2154[d]				[23]
	[{MeB[3-(C_2F_5)pz]$_3$}Ag(CO)]	2153[e]	2.030(4)	2.314(3)	1.117(4)	[3]
	[{HB[3,4,5-(Br)$_3$pz]$_3$}Ag(CO)]	2153[f]				[24]
	[{HB[3-(CF_3),5-(Ph)pz]$_3$}Ag(CO)]	2149[g]				[17]
	free CO	**2143**			**1.1283**	[25]
Classical	[{CpCo[P(O)(OEt)$_2$]$_3$}Ag(CO)]	2125[g] *(2147)*[h]				[21]
	[{MeB[3-(Mes)pz]$_3$}Ag(CO)] (**2**)	2125[e] 2128[g]	1.994(3)[c]	2.305(2)	1.111(4)[c]	this study

[a] The presence of a ν_{CO} band in solution is the only evidence for the existence of some of these compounds. Bond distances are given for compounds that have been characterized structurally. [b] Nujol. [c] Average value. [d] CH_2Cl_2. [e] KBr. [f] THF. [g] Hexane. [h] MeOH.

The ethylene group of **1** is labile in solution; in C_6D_{12}, the ^{1}H NMR spectrum contains a signal at $\delta = 3.40$ ppm which corresponds to the ethylene moiety. Addition of free C_2H_4 to the solution led to the coalescence of the bound ethylene signal. This signal reappeared on purging the solution with N_2 (to remove the excess free ethylene). The ^{13}C NMR signal corresponding to the bound ethylene appears as a broad signal at $\delta = 95.4$ ppm.

Complex **1** is a good precursor to obtain the corresponding Ag^I–CO adduct. The treatment of **1** with carbon monoxide in hexane led to [{MeB[3-(Mes)pz]$_3$}Ag(CO)] (**2**, Figure 1) in quantitative yield. The removal of the solvent under reduced pressure from concentrated solutions of **2** does not lead to the loss of coordinated carbon monoxide but the carbonyl adducts tend to lose carbon monoxide from dilute solutions. However, solid **2** shows remarkable stability; for example, a solid sample of **2** stored in a sealed dark vial (filled with air) at room temperature showed a ν_{CO} band in the IR spectrum even after 60 days.

The FTIR spectrum of **2** in KBr displays a strong band at 2125 cm^{-1} (2128 cm^{-1} in hexane; 2129 cm^{-1} in CH_2Cl_2) that can be assigned to ν_{CO}. This value is lower than that observed for free CO (2143 cm^{-1}, Table 1). As indicated earlier, all the Ag^I–CO compounds that have been structurally characterized thus far show nonclassical behavior ($\tilde{\nu}_{CO} > 2143$ cm^{-1}).[5] There is one report that describes the existence of [{CpCo[P(O)(OEt)$_2$]$_3$}Ag(CO)] with the ν_{CO} band appearing in the classical carbonyl region (2125 cm^{-1} in hexane),[21] although the ν_{CO} band in methanol appears at 2147 cm^{-1}. In any event, apart from the IR data of the complex in solution, this molecule has not been isolated or fully characterized.

Compound **2** crystallizes in the $P2_1/n$ space group with two chemically similar but crystallographically different molecules in the asymmetric unit. The silver atom adopts a distorted tetrahedral geometry (Figure 3). The average Ag–N bond distance is marginally shorter than those in the ethylene adduct **1**. The Ag-C-O moiety is not exactly linear (average angle 170.3(4)°) and the average Ag–C bond of 1.994(3) Å is slightly shorter than those reported for [{MeB[3-(C_2F_5)pz]$_3$}Ag(CO)] and [{HB[3,5-(CF_3)$_2$pz]$_3$}Ag(CO)] (2.030(4) and 2.037(5) Å, respectively). This could be a sign of increased π backbonding in the Ag–CO complex bearing the more electron-rich [MeB{3-(Mes)pz}$_3$]$^-$ ligand, which is consistent with the observed $\tilde{\nu}_{CO}$ value.[17]

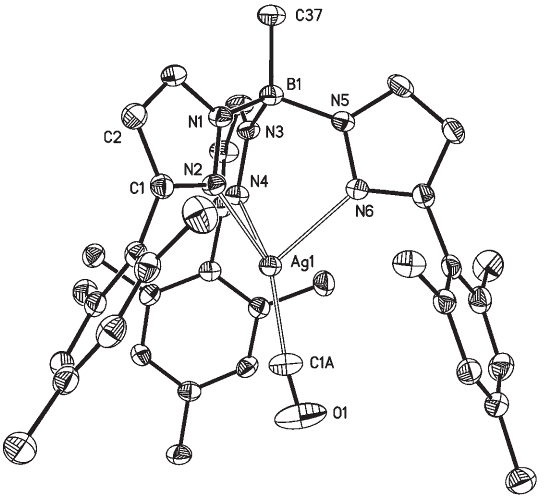

Figure 3. Molecular structure of **2**. All hydrogen atoms and the second molecule in the asymmetric unit have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1-C1A 1.995(3), Ag1-N6 2.295(2), Ag1-N4 2.297(2), Ag1-N2 2.316(2), C1A-O1 1.111(4), Ag1···B1 3.393, O1-C1A-Ag1 171.3(4), C1A-Ag1···B1 167.62; (Measurements for the second molecule: Ag2-C2A 1.992(3), Ag2-N8 2.287(2), Ag2-N12 2.312(2), Ag2-N10 2.324(2), C2A-O2 1.112(4), Ag2···B2 3.367, O2-C2A-Ag2 169.2(4), C2A-Ag2···B2 166.25). Thermal ellipsoids are set at the 35% probability level.

Preliminary data indicate that it is also possible to prepare the corresponding Cu^I and Au^I adducts.[18] The ν_{CO} band of [{MeB[3-(Mes)pz]$_3$}Cu(CO)] appears in the IR spectrum at 2075 cm^{-1} (KBr) whereas for [{MeB[3-(Mes)pz]$_3$}Au(CO)], this band appears at 2083 cm^{-1} (hexane). This group trend of

$\tilde{\nu}_{CO}(Cu) < \tilde{\nu}_{CO}(Au) < \tilde{\nu}_{CO}(Ag)$ is in excellent agreement with both theoretical and experimental data already reported in the literature,[5,20] and clearly shows that the $M \rightarrow L$ π back donation decreases from Cu^I to Ag^I and increases again from Ag^I to Au^I.

In conclusion, we have shown that it is possible to synthesize and isolate thermally stable Ag–CO and Ag–C_2H_4 adducts using a nonfluorinated, electron-rich ligand $[MeB\{3\text{-(Mes)pz}\}_3]^-$, and compound **2** is the first structurally characterized classical silver carbonyl complex.

Experimental Section

1: ^{1}H NMR ($CDCl_3$, 298 K): $\delta = 1.13$ (s, 3H, BCH_3), 1.86 (s, 18H, o-CH_3), 2.21 (s, 9H, p-CH_3), 3.42 (s, 4H, $CH_2{=}CH_2$), 6.00 (d, 3H, $^3J_{HH} = 2.0$ Hz, C4H), 6.77 (s, 6H, m-CH), 7.78 ppm (d, 3H, $^3J_{HH} = 2.0$ Hz, C5H); ^{1}H NMR (C_6D_{12}, 298 K): $\delta = 1.13$ (s, 3H, BCH_3), 1.86 (s, 18H, o-CH_3), 2.18 (s, 9H, p-CH_3), 3.40 (s, 4H, $CH_2{=}CH_2$), 5.89 (d, 3H, $^3J_{HH} = 2.0$ Hz, C4H), 6.69 (s, 6H, m-CH), 7.72 ppm (d, 3H, $^3J_{HH} = 2.0$ Hz, C5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): $\delta = 5.0$ (br s, BCH_3), 20.6, 21.1, 95.4 (br s, $CH_2{=}CH_2$), 103.6, 127.7, 132.9, 133.1, 137.1, 138.0, 150.3. Crystal data for **1**: $C_{39}H_{46}N_6AgB$, rhombohedral, $R3c$; 100 K; $a = b = 12.0079(5)$, $c = 43.861(2)$ Å, $V = 5477.0(4)$ Å^3, $Z = 6$; $R1$, $wR2$ $(I > 2\sigma(I)) = 0.0176$, $wR2 = 0.0452$.

2: FTIR: $\tilde{\nu}_{CO} = 2125\ cm^{-1}$ (KBr pellets, the ^{13}CO satellite was observed at $2079\ cm^{-1}$, resolution $1\ cm^{-1}$); $2128\ cm^{-1}$ (hexane, resolution $2\ cm^{-1}$); $2126\ cm^{-1}$ (nujol, resolution $2\ cm^{-1}$); $2129\ cm^{-1}$ (CH_2Cl_2, resolution $2\ cm^{-1}$); ^{1}H NMR (C_6D_{12}, 298 K): $\delta = 1.11$ (s, 3H, BCH_3), 1.86 (s, 18H, o-CH_3), 2.15 (s, 9H, p-CH_3), 5.91 (d, 3H, $^3J_{HH} = 2.0$ Hz, C4H), 6.69 (s, 6H, m-CH), 7.70 ppm (d, 3H, $^3J_{HH} = 2.0$ Hz, C5H). Crystal data for **2**; $C_{38}H_{42}N_6AgBO$, monoclinic, $P2_1/n$; 198 K; $a = 24.2090(17)$, $b = 11.2923(8)$, $c = 26.8553(19)$ Å; $\beta = 100.8030(10)°$, $V = 7211.5(9)$ Å^3, $Z = 8$; $R1$, $wR2$ $(I > 2\sigma(I)) = 0.0402$, $wR2 = 0.0907$.

1 from **2**: Ethylene was bubbled through a solution of **2** in hexane at room temperature to give the corresponding ethylene adduct in quantitative yield.

CCDC-622971 and CCDC-622972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] C. Elschenbroich, *Organometallics*, 3rd ed., VCH, Weinheim, **2006**.
[2] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, 3rd ed., VCH, Weinheim, **1997**.
[3] H. V. R. Dias, X. Wang, *Dalton Trans.* **2005**, 2985–2987, and references therein.
[4] M. C. Gimeno, A. Laguna, *Comprehensive Coordination Chemistry II, Vol. 6*, Elsevier, Oxford, **2004**, pp. 911–1145.
[5] A. J. Lupinetti, S. H. Strauss, G. Frenking, *Prog. Inorg. Chem.* **2001**, *49*, 1–112, and references therein.
[6] J. P. Fackler, Jr. in *Encyclopedia of Inorganic Chemistry*, *Vol. 7* (Ed.: R. B. King), Wiley, New York, **1987**, pp. 3829–3834.
[7] I. Krossing, A. Reisinger, *Angew. Chem.* **2003**, *115*, 5903–5906; *Angew. Chem. Int. Ed.* **2003**, *42*, 5725–5728, and references therein.
[8] P. K. Hurlburt, J. J. Rack, S. F. Dec, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1993**, *32*, 373–374.
[9] P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *J. Am. Chem. Soc.* **1991**, *113*, 6277–6278.
[10] H. V. R. Dias, W. Jin, *J. Am. Chem. Soc.* **1995**, *117*, 11381–11382.
[11] H. V. R. Dias, Z. Wang, W. Jin, *Inorg. Chem.* **1997**, *36*, 6205–6215.
[12] H. A. Chiong, O. Daugulis, *Organometallics* **2006**, *25*, 4054–4057.
[13] A. J. Lupinetti, G. Frenking, S. H. Strauss, *Angew. Chem.*, **1998**, *110*, 2229–2232; *Angew. Chem. Int. Ed.* **1998**, *37*, 2113–2116.
[14] H. V. R. Dias, X. Wang, *Polyhedron* **2004**, *23*, 2533–2539.
[15] H. V. R. Dias, H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browning, C. J. Lovely, *Organometallics* **2002**, *21*, 1466–1473, and references therein.
[16] M. Munakata, S. Kitagawa, S. Kosome, A. Asahara, *Inorg. Chem.* **1986**, *25*, 2622–2627.
[17] H. V. R. Dias, T. K. H. H. Goh, *Polyhedron* **2004**, *23*, 273–282.
[18] H. V. R. Dias, M. Fianchini, unpublished results.
[19] J. S. Thompson, R. L. Harlow, J. F. Whitney, *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527.
[20] H. V. R. Dias, W. Jin, *Inorg. Chem.* **1996**, *35*, 3687–3694.
[21] B. Lenders, W. Kläui, *Chem. Ber.* **1990**, *123*, 2233–2240.
[22] P. K. Hurlburt, J. J. Rack, J. S. Luck, S. F. Dec, J. D. Webb, O. P. Anderson, S. H. Strauss, *J. Am. Chem. Soc.* **1994**, *116*, 10003–10014.
[23] D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, G. P. A. Yap, *Organometallics* **1997**, *16*, 349–353.
[24] J. Urbano, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, M. M. Diaz-Requejo, P. J. Perez, *Organometallics* **2005**, *24*, 1528–1532.
[25] G. Frenking, C. Loschen, A. Krapp, S. Fau, S. H. Strauss, *J. Comput. Chem.* **2007**, *28*, 117–126, and references therein.