Figure 1. (—) EXAFS (xk^2) associated with the Cd K-edge of Rat Liver Cd/Zn-metallothionein 1 and its Fourier transform. (- - -) Simulated data for four Cd-S distances of 2.53 Å with a Debye–Waller parameter of 0.013 Å^2.

monochromator was used and data were recorded from 300 eV before the cadmium K-absorption edge up to 1500 eV beyond the edge. Several (ca. four) scans were recorded for each sample and the data were averaged. No signs of radiation-induced damaged were observed (i.e., the spectrum did not change upon exposure to the X-rays). Data analysis, utilizing the single-scattering spherical-wave method for calculating the EXAFS with phase-shifts derived from ab initio calculations,[11-13] the determination of the quality of fit, and the refinement were accomplished as described previously.[14]

No significant difference was detected between the EXAFS associated with the cadmium K-edge of Cd/Zn-metallothionein 1 and that for Cd-metallothionein 1. The EXAFS ($\times k^2$) associated with the cadmium K-edge of Cd/Zn-metallothionein 1, a successful simulation, and the corresponding Fourier transforms are shown in Figure 1. The cadmium K-edge EXAFS of Cd/Zn- and Cd-metallothionein 1 are consistent with each cadmium atom having an environment consisting of a single shell of four sulfur atoms at 2.53 (2) Å. No indication of any Cd···Cd back-scattering was manifest in the EXAFS and the introduction of oxygen or nitrogen back-scattering contributions at chemically reasonable distances significantly deteriorated the quality of the agreement between the stimulated and the experimental data. The reliability of the EXAFS interpretation receives justification from the 2.52 (1) Å obtained for the Cd-S distance in CdS, as compared with the crystallographic value of 2.52 Å.[15] The Cd-S distance and

coordination number obtained for cadmium in metallothionein 1 are not unexpected, given the known thiolate chemistry of this element.[16]

The structural information presented herein strengthens the interpretation of the ^{113}Cd NMR data obtained for metallo-thioneins[5-9] and is compatible with the proposals of Otvos and Armitage.[8] The EXAFS results demonstrate that the chemical inequivalence observed by ^{113}Cd NMR does not arise from marked variations in atom type, coordination number, or metal-ligand distances within the metals' first coordination sphere. Small differences (ca. 0.02 Å) between Cd-S distances, perhaps due to the presence of bridging and terminal thiolato groups, would be consistent with the EXAFS data.

(16) Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3171-3174.

Ligand-Induced Reactions of a Directly Bonded Early-Late Transition-Metal Complex Involving Reversible Cleavage of a Zr-Ru Bond with Expulsion of a Ruthenium Hydride

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Heterobimetallic complexes in which an early transition metal is directly bonded to a late transition metal are interesting as potential precursors of new types of hydrogenation catalysts. Recently we reported the synthesis of a series of metal-metal-bonded zirconium-iron and zirconium-ruthenium complexes[1] and of the novel zirconium-diruthenium complex $(C_5H_5)_2Zr[Ru(C-O)_2(C_5H_5)]_2$ (1).[2] Here we report the unprecedented reactions of 1 with added ligands that lead to expulsion of $(C_5H_5)Ru(CO)_2H$ and formation of C_5H_4Zr products or intermediates.

When a dark-orange C_6D_6 solution of 1 under 700 mm of CO was monitored by ^1H NMR, the slow ($t_{1/2} \sim$ 3 h) formation of $(C_5H_5)Ru(CO)_2H$ and a new heterobimetallic complex 2 containing two equivalent Cp's on Zr (δ 5.10) and a mirror-symmetric C_5H_4 ligand (δ 4.78, 3.93) was observed and the solution became light orange. When a slurry of 1 (140 mg) in 1:1 toluene/ether was stirred under CO for 48 h, 2 (70 mg, 70%) precipitated from solution as a yellow powder.

The structure of 2 was determined by X-ray crystallography[3] (Figure 1). The Zr and Ru centers of 2 are linked both by a metal-metal bond and by a bond from Zr to the η^5-C_5H_4 ligand on Ru. This Zr-C bond is bent 34° below the plane of the C_5H_4 ligand.[4] The zirconium-bound CO is bent slightly away from Ru (Zr-C-O 167°) indicating a very weak interaction with the remote (2.70 Å) Ru.

When a C_6D_6 solution of 1 was treated with PMe$_3$, the formation of $(C_5H_5)Ru(CO)_2H$ and a new heterobimetallic com-

(11) Lee, P. A.; Pendry, J. B. *Phys. Rev.* **1975**, *B11*, 2795-2811.

(12) Perutz, M. F.; Hasnain, S. S.; Duke, P. J.; Sessler, J. L.; Hahn, J. E. *Nature (London)* **1982**, *295*, 535-538.

(13) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C* **1984**, *17*, 143-151.

(14) Blackburn, N. J.; Hasnain, S. S.; Diakun, G. P.; Knowles, P. F.; Binsted, N.; Garner, C. D. *Biochem. J.* **1983**, *213*, 765-768.

(15) Wyckoff, R. W. G.; "Crystal Structures"; Wiley: New York, 1965; Vol. 1, p 110.
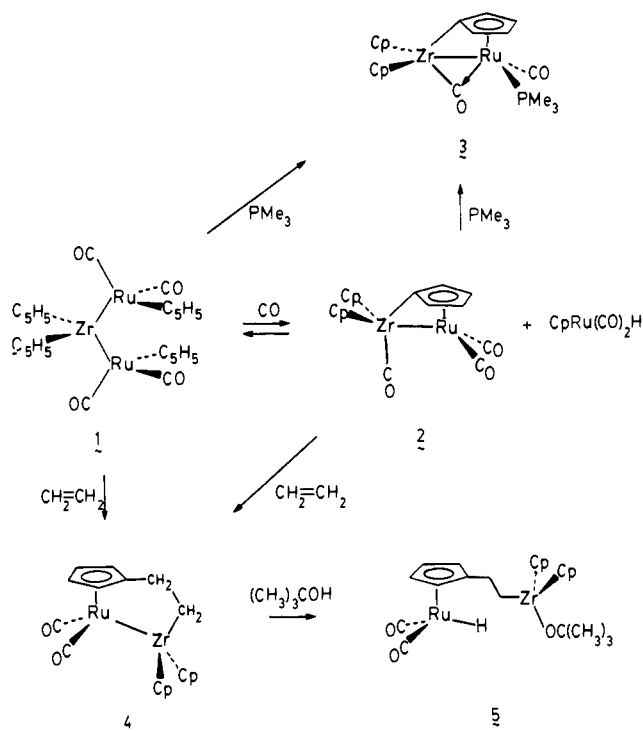
(1) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.

(2) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

(3) See supplementary material for spectroscopic characterization and for X-ray structure determinations of 2 and 3.

(4) (a) Lemenovskii, D. A.; Fedin, V. P.; Aleksandrov, A. V.; Slovohotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1980**, *201*, 257. (b) Bashkin, J.; Green, M. L. H.; Poveda, M. L.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1982**, 2485 and references therein.

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Communications to the Editor

Figure 1. Molecular structure and labeling scheme for Cp₂Zr(CO)(μ-η¹(Zr),η⁵-C₅H₄)Ru(CO)₂ (2). The crystallographic mirror plane contains Zr, Ru, O(2), C(2), and C(21). Additional distances (Å) and angles (deg): Ru–C(2), 2.701 (6); Zr–C(2)–O(2), 166.7 (5); Ru–C(2)–O(2), 117.3 (4); Ru–C(2)–Zr, 76.0 (4); C(2)–Zr–C(21), 103.8 (2); C(2)–Zr–Ru, 58.8 (1); C(21)–Zr–Ru, 45.0 (1); CNT(Zr)–Zr–CNTa(Zr), 131.1 (2). CNT indicates the centroid of a Cp ring.

pound **3** with two nonequivalent (C₅H₅)Zr ligands and a nonmirror symmetric C₅H₄ ligand was observed by ¹H NMR.[3] **3** was isolated as red microcrystals in 36% yield by reaction of **1** with PMe₃ in toluene and was characterized by X-ray diffraction[3] (Figure 2). In **3**, the interaction of the more electron rich phosphine-substituted Ru with the Zr-bound CO is substantially stronger than in **2**. The 2.21-Å Ru–μ-C(2)O bond length is 0.5 Å shorter than in **2** but still substantially longer than the 2.00-Å Ru-bridging CO distance in [CpRu(CO)]₂(μ-CO)₂.[5] The Zr–C(2)–O(2) angle of 145° and the Ru–C(2)–O(2) angle of 127° in **3** are also consistent with a semibridging interaction with Ru. The substantially greater interaction between Ru and the zirconium carbonyl in **3** relative to **2** results in a lower CO IR stretching frequency for **3** (1670 vs. 1840 cm⁻¹ for **2**) and a farther downfield ¹³C chemical shift for the more strongly bridging CO of **3** (δ 331 vs. 277 for **2**). In both compounds, the carbon of the C₅H₄ ligand directly bonded to Zr appears unusually far downfield at δ 193 for **2** and 187 for **3**.

1 reacts with ethylene (700 mm) in C₆D₆ to produce CpRu-(CO)₂H and **4** which incorporates 1 equiv of ethylene. The structure of **4** was established by spectroscopy[6] and by derivatization with *t*-BuOH. **4** contains a mirror symmetric C₅H₄ unit but this unit cannot be bonded to Zr since the unique carbon of the ligand appears at δ 110 in the ¹³C NMR and not far downfield as in the case of **2** and **3**. The presence of a direct Zr–Ru bond in **4** is established by the similarity of the IR stretches of **4** at 1948 and 1888 cm⁻¹ to those seen for Cp₂Zr(CH₃)Ru(CO)₂Cp. The ethylene unit bridges between the C₅H₄ ligand and Zr and gives rise to an AA'XX' pattern in the ¹H NMR at δ 0.28 and 2.18. The Zr–Ru bond of **4** is cleaved by reaction with *t*-BuOH; this produces complex **5** which contains a new *tert*-butoxyzirconium unit and a new ruthenium hydride and retains the C₅H₄–CH₂C-H₂–Zr unit.[7]

The carbonylation product **2** is particularly reactive. Surprisingly, isolated **2** reacts with CpRu(CO)₂H in toluene–THF to regenerate starting material **1** in greater than 50% yield. The
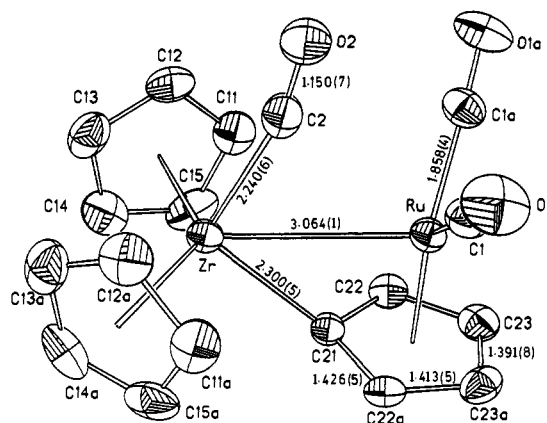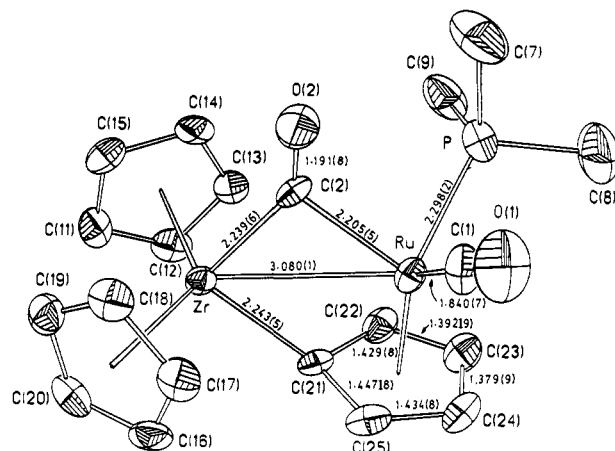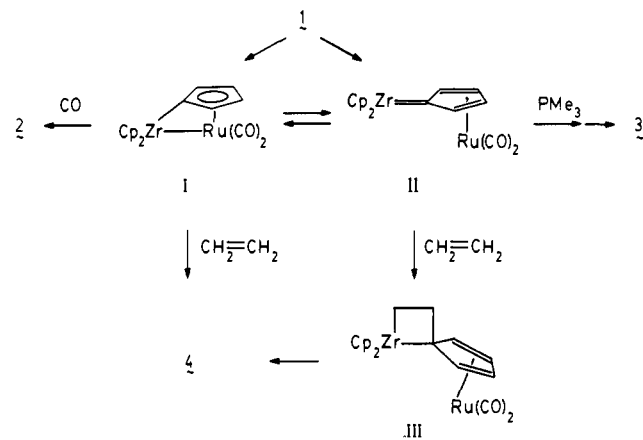
Figure 2. Molecular structure and labeling scheme for Cp₂Zr(CO)(μ-η¹(Zr),η⁵-C₅H₄)Ru(PMe₃)(CO) (3). Additional distances (Å) and bond angles (deg): Zr–C(2)–O(2), 144.8 (4); Ru–C(2)–O(2), 127.2 (4); Ru–C(2)–Zr, 87.7 (2); C(2)–Zr–C(21), 92.5 (2); C(2)–Zr–Ru, 45.7 (1); C(21)–Zr–Ru, 46.9 (2); CNT(Zr)–Zr–CNT'(Zr), 129.5 (3).

Scheme I

Zr-bound carbonyl of **2** exchanges instantaneously with ¹³CO at 0 °C. Reaction of **2** with PMe₃ produces **3** and reaction with ethylene produces **4**. The high reactivity of **2** is attributed to the ready dissociation of CO and to the strained nature of the C₅-H₄ZrRu ring system.

We believe that intermediate I may be involved in all these reactions (Scheme I). I could be formed directly from **1** by

(5) (a) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339. (b) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43.

(6) **4**: ¹H NMR (C₆D₆) δ 5.91 (s, Cp₂Zr), 4.75 (t, *J* = 2 Hz, 2 H), 4.19 (t, *J* = 2 Hz, 2 H) (C₅H₄), 2.18 (2 H, ZrCCH₂), 0.28 (2 H, ZrCH₂).[3]

(7) **5**: ¹H NMR (C₆D₆) δ 5.71 (s, Cp₂Zr), 4.98 (t, *J* = 2 Hz, 2 H), 4.69 (t, *J* = 2 Hz, 2 H) (C₅H₄), 2.50 (2 H, ZrCCH₂), 1.04 (2 H, ZrCH₂), 0.9 (s, OC(CH₃)₃), -10.27 (s, RuH).[3]

elimination of CpRu(CO)$_2$H or via migration of Zr to the C$_5$H$_5$ ligand bound to Ru followed by β-hydride elimination to give II and ring closure to I. Reversible addition of CO to I explains the formation and ^{13}CO exchange of **2**. Intermediate II has a vacant site at Ru that can be captured by PMe$_3$ to eventually produce **3**. The formation of ethylene adduct **4** can be explained either by insertion of ethylene into the reactive strained Zr–C$_5$H$_4$ bond of I or by reaction of ethylene with II to give metallacyclobutane intermediate III.

Supplementary Material Available: Spectroscopic data for **2–5** and details of the X-ray structure solutions for **2** and **3**, with listings of fractional coordinates and thermal parameters, bond distances, and bond angles (9 pages). Ordering information is given on any current masthead page.

Coordination of a "Noncoordinating" Anion: X-ray Crystal Structure and ^{31}P NMR Characterization of a Tungsten Nitrosyl Cation Ligated to SbF$_6^-$

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A large body of research on the spectral characterization of carbocations in superacid media has shown that these species are present as fully ionized cations.[1] The simplest of the many noncoordinating anions that are present in these media is the hexafluoroantimonate ion, SbF$_6^-$.[2] The coordinating ability of this anion must be exceedingly poor, and in fact it is known to give covalent adducts only with CH$_3^+$ and SbF$_5$, resulting in the monofluorine-bridged species CH$_3$FSbF$_5$[1d,3] and Sb$_2$F$_{11}^-$.[2] A number of examples of adducts involving other "noncoordinating" anions, including ClO$_4^-$, BF$_4^-$, PF$_6^-$, and AsF$_6^-$, are known; in these cases the Lewis acid acceptors are transition metals.[4] We report here what we believe to be the first example of coordination of SbF$_6^-$ to a transition metal, including an X-ray diffraction study, NMR evidence that the solid-state coordination persists in solution, and a novel fluctional process in which the SbF$_6^-$ ligand apparently "spins" while remaining in the coordination sphere of the metal.

As part of a project whose goal is the high-yield synthesis of tungsten mononitrosyl carbonyl complexes,[5] we combined various
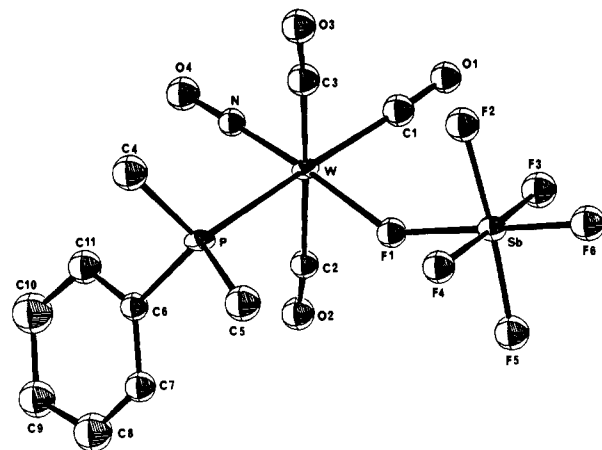

Figure 1. ORTEP drawing of Me$_2$PhP(CO)$_3$(NO)W(μ-F)SbF$_5$ (**1a**). Selected bond distances (Å) and angles (deg): W–P, 2.518 (5); W–N, 1.795 (17); W–C(1), 2.092 (23); W–C(2), 2.089 (20); W–C(3), 2.052 (21); F(1)–W–N, 176.51 (57); P–W–C(1), 175.36 (61); C(2)–W–C(3), 176.49 (82); F(1)–W–P, 86.43 (32); F(1)–W–C(1), 89.47 (68); F (1)–W–C(2), 89.32 (62); F(1)–W–C(3), 89.08 (67).

tungsten phosphine complexes with NO$^+$SbF$_6^-$. While Ph$_3$PW-(CO)$_5$, as does W(CO)$_6$,[6b] gave mainly carbonyl-free tungsten dinitrosyl dications,[6] the use of more basic phosphine ligands such as Me$_2$PhP and Me$_3$P resulted in rapid and clean consumption of starting material via reaction with a single equivalent of NO$^+$SbF$_6^-$. The infrared spectrum of the Me$_2$PhP adduct **1a**, for

1a L = Me$_2$PhP
1b L = Me$_3$P
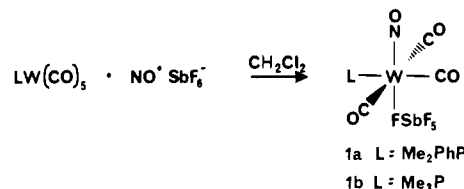
instance, showed bands at 2102 (m), 2012 (s), and 1690 (s) cm^{-1} due respectively to two carbonyl ligands trans to each other, another cis carbonyl, and a single nitrosyl ligand,[7] while the ^{1}H NMR indicated the presence of a single bound phosphine ligand. Isolation of **1a** and **1b** as yellow crystalline compounds[8] allowed for more definitive characterization.[9] In particular, the mass spectra indicated the coordination of SbF$_6^-$: while no molecular ions were observed, WSb envelopes[10] due to M$^+$–CO and M$^+$–2CO

(1) (a) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360–1373. (b) Olah, G. A.; White, A. M. *Ibid.* **1969**, *91*, 5801–5810. (c) Kirchen, R. P.; Sorensen, T. S. *Ibid.* **1977**, *99*, 6687–6693. (d) Olah, G. A.; Donovan, D. J. *Ibid.* **1978**, *100*, 5163–5169. (e) Arnett, E. M.; Petro, C. *Ibid* **1978**, *100*, 5408–5416.

(2) While the precise concentrations of the various anions depend on the reaction conditions, SbF$_6^-$ can be a major component in SbF$_5$–HSO$_3$F ("magic acid") systems, although Sb$_2$F$_{11}^-$ is the simplest anion present in media containing SbF$_5$ as the only acid: (a) Commeyras, A.; Olah, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 2929–2942. (b) Bacon, J.; Dean, P. A. W.; Gillespie, R. J. *Can. J. Chem.* **1969**, *47*, 1655–1659.

(3) Calves, J.-Y.; Gillespie, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 1788–1792.

(4) (a) Mayfield, H. G.; Bull, W. E. *J. Chem. Soc. A* **1971**, 2279–2281. (b) Mews, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 640. (c) Richter, K.; Fischer, E. O.; Kreiter, C. G. *J. Organomet. Chem.* **1976**, *122*, 187–196. (d) Beck, W.; Schloter, K. *Z. Naturforsch., B* **1978**, *33B*, 1214–1222. (e) Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* **1978**, *31*, 267–278. (f) Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803–3807. (g) Mattson, B. M.; Graham, W. A. G. *Ibid.* **1981**, *20*, 3186–3189. (h) Raab, K.; Olgemoller, B.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1981**, *214*, 81–86. (i) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785–1791.

(5) Mononitrosyl tungsten carbonyl complexes are available in low overall yield (a–e) and with chelating phosphine ligands (f): (a) Barraclough, C. G.; Bowden, J. A.; Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 241–245. (b) Colton, R.; Commons, C. J. *Ibid.* **1973**, *26*, 1487–1492. (c) King, R. B.; Saran, M. S.; Anand, S. P. *Inorg. Chem.* **1974**, *13*, 3038–3040. (d) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *99*, 119–126. (e) Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875–1878. (f) Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1973**, 2183–2188.

(6) (a) Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1972**, 2629–2631. (b) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251–1254.

(7) The tungsten dinitrosyl dications referred to in ref 6 typically exhibit nitrosyl bands at 1730–1870 cm^{-1}, and at most a single carbonyl band around 2160 cm^{-1}, while the mononitrosyl adducts in ref 5 give corresponding bands at 1670–1725 and 2090–2145 cm^{-1}.

(8) A typical procedure is as follows: in an inert atmosphere glovebox, powdered NO$^+$SbF$_6^-$ (0.58 g) was added to 1.01 g of Me$_2$PhPW(CO)$_5$ in 25 mL of CH$_2$Cl$_2$. The stirred solution was maintained under a partial vacuum for 1 h, after which it was concentrated to 10 mL and filtered. After addition of 25 mL of CCl$_2$FCClF$_2$ and cooling to –40 °C, the yellow suspension was filtered and the solution concentrated until a precipitate (of **1a**) was observed, ca. 15–20 mL. Cold hexanes (25 mL) was layered on, and the mixture cooled to –40 °C overnight. After filtering and washing with hexanes, 0.96 g (66% yield) of bright yellow crystals of **1a** were obtained. Both **1a** and **1b** are somewhat air and temperature sensitive, as well as extremely hygroscopic.

(9) **1a**: IR (CH$_2$Cl$_2$) 2102 (m), 2012 (s), 1690 (s) cm^{-1}; ^{1}H NMR (C-D$_2$Cl$_2$) δ 7.55–7.59 (m, 5 H), 2.078 (d, J = 8.9 Hz, 6 H); MS (EI), m/e (for ^{184}W, ^{121}Sb, L = Me$_2$PhP) 643 (L(CO)$_2$(NO)WFSbF$_5^+$), 615 (L(CO)-(NO)WFSbF$_5^+$), 436 (L(CO)$_3$(NO)W$^+$), 427 (L(CO)$_2$(NO)WF$^+$, weak), 399 (L(CO)(NO)WF$^+$), 371 (L(NO)WF$^+$), 341 (LWF$^+$); Anal. Calcd for C$_{11}$H$_{11}$NO$_4$PSbF$_6$W: C, 19.67; H, 1.65; N, 2.09. Found: C, 19.62; H, 1.54, N, 2.04. **1b**: IR (CH$_2$Cl$_2$) 2102 (m), 2010 (s), 1690 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.804 (d, J = 9.5 Hz); MS (EI), m/e (for L = Me$_3$P) 581 (L(CO)$_2$(NO)WFSbF$_5^+$), 553 (L(CO)(NO)WFSbF$_5^+$), 374 (L(CO)$_3$-(NO)W$^+$), 365 (L(CO)$_2$(NO)WF$^+$, weak), 337 (L(CO)(NO)WF$^+$), 309 (L(NO)WF$^+$); Anal. Calcd for C$_6$H$_9$NO$_4$PSbF$_6$W: C, 11.82; H, 1.49; N, 2.30; P, 5.08; F, 18.70. Found: C, 11.58; H, 1.65; N, 2.38; P, 5.16; F, 18.47.

(10) Tungsten has four abundant isotopes, antimony two; see, e.g.: Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 88.