Bis[2-((dimethylamino)methyl)ferrocenyl]lead, $(FcN)_2Pb$, as a Ligand: Synthesis and Characterization of the Heterotrimetallic Metalloplumbylene Compounds $(FcN)_2PbM(CO)_5$ (M = Cr, Mo, W)

Naka Seidel,† Klaus Jacob,*,† and Axel K. Fischer‡

Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg,
Geusaer Strasse 88, D-06217 Merseburg, Germany, and Chemisches Institut der
Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39333 Magdeburg, Germany

Received September 15, 2000

Summary: The reaction of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3(CH_2NMe_2)\text{-}2)\text{-}C,N]_2Pb$*,* $(FcN)_2Pb$ *(**1**), with the group 6 carbonyl derivatives* $M(CO)_5L$ *(M = Cr, W, L = THF; M = Mo, L = THF,* NMe_3*) affords the heterotrimetallic plumbylene adducts* $(FcN)_2PbM(CO)_5$ *(M = Cr (**2**), Mo (**3**), W (**4**)) in excellent yield. All compounds were characterized by elemental analysis, X-ray crystallography, and IR and* ^1H *and* ^{13}C *NMR spectroscopy. The results show that the metalloplumbylenes **2**−**4** exist solely as meso diastereomers, both in the solid state and in solution, although the starting compound **1** consists in solution of a mixture of two interconverting diastereomers, rac- and meso-*$(FcN)_2Pb$*. The Pb−M bond lengths are indicative of some degree of π-bonding.*

Introduction

The chemistry of plumbylenes—the lead analogues of the carbenes—was until recently not investigated to any great extent.[1] Compounds that contain bonds between lead(II) and transition metals are exceptionally rare. In terms of the character of the lead−transition-metal bonding, these compounds can be divided into two categories: those possessing either pure σ-bonds, such as $\{Mo(R)(CO)_3\}_2Pb\cdot THF$ (R = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ or $\eta^5\text{-}C_5Me_5$),[2] (salen)$PbM(CO)_5$ (M = Cr, W),[3] (bipy)$Pb\{Cr(CO)_5\}_2$,[4] and, most recently, $(\eta^5\text{-}C_5H_5)(CO)_3M{-}Pb{-}C_6H_3\text{-}2,6\text{-}Trip_2$ (M = Cr, Mo, W; Trip = $C_6H_2{-}2,4,6\text{-}i Pr_3$)[5] and $\{W(CO)_4\}_2(\mu\text{-}Br)(\mu\text{-}PbC_6H_3\text{-}2,6\text{-}Trip_2)$,[6] or those featuring a donor-type σ-bond, such as the spectroscopically characterized $(CO)_5MoPb\{CH(SiMe_3)_2\}_2$[1b] and $Pd(\eta^5\text{-}C_5H_5)(CO)_3(\mu\text{-}Cl)Pb\{N(SiMe_3)_3\}$.[7] Compounds of the latter type are thought to have some degree of π-backbonding, but this has not been structurally demonstrated until now.

Recently, we have synthesized the heterobimetallic plumbylene compound $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3(CH_2NMe_2)\text{-}2)\text{-}C,N]_2Pb$ (**1**), stabilized by intramolecular Pb−N interactions.[8] **1** bears a stereochemically active lone pair, as well as empty p-orbitals with π-symmetry, and should therefore be able to act as a carbene-like ligand. We decided to study the Lewis-base behavior of this compound toward group 6 metal carbonyls. This yielded the first structurally characterized heterotrimetallic metalloplumbylenes of the type in which the $(FcN)_2Pb$ moiety behaves as a ligand.

Results and Discussion

The title species **2**−**4** were synthesized in excellent yields in a straightforward manner by the reaction of **1** with $M(CO)_5L$ (M = Cr, W, L = THF; M = Mo, L = THF, NMe_3) (Scheme 1). The orange crystals, grown from pentane, are moderately air- and light-sensitive. However, in solution they decompose immediately when exposed to air. **2**−**4** are readily soluble in both polar and nonpolar solvents.

The starting compound **1** consists in solution of a mixture of two interconverting diastereomers, *rac*- and *meso*-$(FcN)_2Pb$.[8] However, all three compounds **2**−**4** exist solely in the form of one diastereomer, *meso*-$(FcN)_2PbM(CO)_5$ (M = Cr (**2**), Mo (**3**), W (**4**)). Obviously, for steric reasons the $M(CO)_5$ species does not react with the *rac* diastereomer and only recognizes *meso*-$(FcN)_2Pb$ for complexation. Because *meso*-$(FcN)_2Pb$ is withdrawn from the equilibrium, the remaining *rac* form is converted to the *meso* diastereomer during the reaction with $M(CO)_5$.

Crystals of **2**−**4** are isomorphous and X-ray diffraction analysis reveals that the compounds also have similar structures (Figure 1). All three compounds crystallize solely as *meso* diastereomers. Selected geometrical data of **2**−**4** are listed in Table 1.

The main feature of interest of all structures concerns the metal−lead distances and the interligand angles at

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* To whom correspondence should be addressed. E-mail: jacob@chemie.uni-halle.de.

† Martin-Luther-Universität Halle-Wittenberg.

‡ Chemisches Institut der Otto-von-Guericke-Universität Magdeburg.

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10.1021/om000796a CCC: $20.00
Publication on Web 01/09/2001

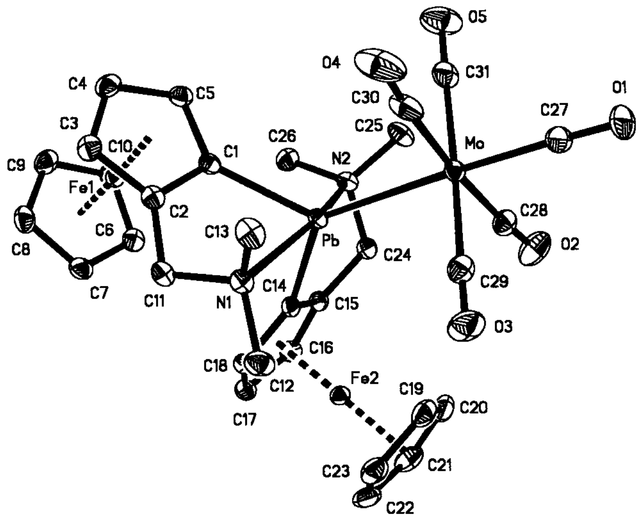

Figure 1. Molecular structure of **3** (ORTEP plot, thermal ellipsoids at 50% probability level). H atoms are omitted for clarity. Selected bond distances and angles are given in Table 1.

Scheme 1

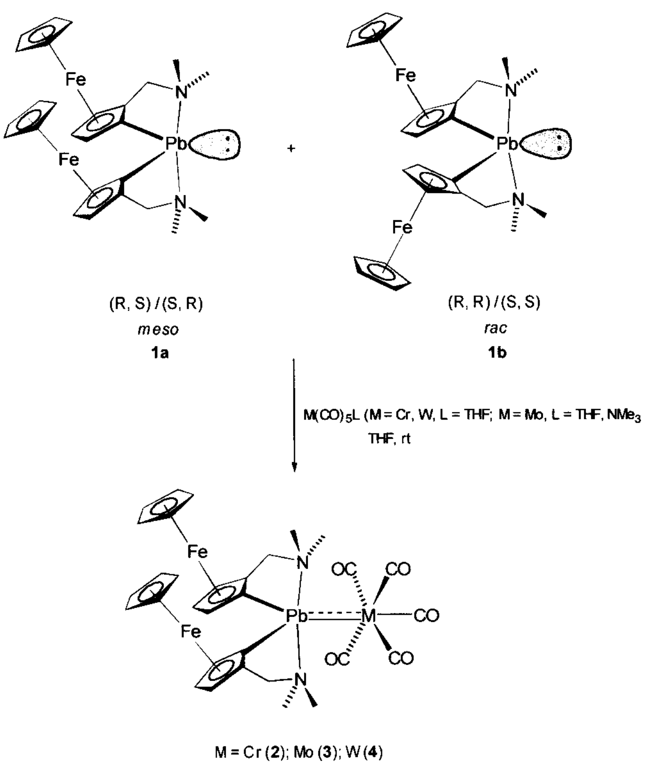

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2−4

	2 (M = Cr)	**3** (M = Mo)	**4** (M = W)
Pb−M	2.7157(4)	2.8531(13)	2.8497(3)
Pb−C1	2.235(3)	2.233(2)	2.241(5)
Pb−C14	2.236(3)	2.234(2)	2.228(5)
Pb−N1	2.676(2)	2.670(2)	2.677(4)
Pb−N2	2.810(4)	2.790(2)	2.793(4)
M−C(CO)$_{cis}$ (av)	1.892(3)	2.044(2)	2.035(6)
M−C(CO)$_{trans}$	1.845(3)	1.986(3)	1.982(6)
M−Pb−C1	127.23(7)	128.13(5)	127.87(13)
M−Pb−C14	133.51(7)	132.78(6)	132.77(13)
M−Pb−N1	103.50(5)	103.21(4)	103.11(10)
M−Pb−N2	97.78	97.72(4)	97.68(9)
C1−Pb−C14	99.19(9)	99.04(8)	99.31(18)
N1−Pb−N2	158.44	158.84(6)	158.96(14)

the lead atom. The lead center essentially has a trigonal-bipyramidal geometry, whereas the transition metal is in a distorted-octahedral environment. The Pb−M bond lengths (M = Cr, 2.7157(4) Å; M = Mo, 2.8531(13) Å; M = W, 2.8497(3) Å) may be compared with those in $Cp(CO)_3M-Pb-C_6H_3$-2,6-$Trip_2$ (M = Cr, 2.9092(9) Å; M = Mo, 2.9845(7) Å; M = W, 2.9809(10)/3.0055(6) Å), which are typical of pure single bonds.[5] The sums of the single-bonded metallic radius of lead (1.54 Å) and the transition-metal radii predict bond lengths of 2.83 Å (Pb−Cr), 2.95 Å (Pb−Mo), and 2.96 Å (Pb−W): the shrinkage of 0.13−0.19 Å for **2**−**4** is indicative of some degree of π-bonding.[9] The Pb−Cr distance in **2** is very close to that in the $[\{(CO)_5Cr\}_3Pb]^{2-}$ anion (2.726(1)−2.733(1) Å), in which there is clear evidence for a Pb−Cr π-bond.[10] The interligand angle C1−Pb−C14 in **2**−**4** (ca. 99.2°) is somewhat larger than the corresponding angles of 94.8(1) and 95.5(2)° found in both polymorphs of **1**[8] and suggests more s-character in the Pb−C bonds. This is corroborated by the fact that these bonds are significantly shorter (Pb−C1/Pb−C14: **2**, 2.235(3)/2.236(3) Å; **3**, 2.233(2)/2.234(2) Å; **4**, 2.241(5)/2.228(5) Å) than in **1** (2.284(4)−2.311(1) Å).[8] The average Pb−N bond lengths (ca. 2.74 Å) in **2**−**4** are about 0.06 Å longer than that in **1**,[8] which is in accord with the greater extent of electronic saturation at the lead center. The average difference between the two Pb−N bond lengths (ca. 0.12 Å) is larger than in **1** (ca. 0.09 and 0.05 Å, respectively)[8] and mirrors the dynamic behavior of **2**−**4** in solution (vide infra). The M−C(CO) bonds trans to the $(FcN)_2Pb$ fragment are ca. 0.05 Å shorter than those of the *cisoid* bonds, suggesting that the $(FcN)_2Pb$ moiety is comparable to or a slightly poorer π-acceptor ligand than CO.

The ^1H and ^{13}C NMR data of **2**−**4**, which show the presence of only one diastereomer, are temperature-dependent, indicating dynamic behavior (Table 2). When the compounds are cooled from room temperature to −80 °C, the single resonance of the methyl groups is split into four signals, whereas the Cp groups appear as two and the C_5H_3 protons as six signals. These data indicate intramolecular dynamics and can be explained by a concerted intramolecular dissociation and recoordination of Pb−N bonds (Scheme 2). This proposal seems even more reasonable, taking into account different Pb−N bond lengths observed in the crystal structures.

The ^{13}C NMR spectra of **2**−**4** feature signals with the characteristic chemical shifts of the carbon atoms of the FcN ligand, shifted slightly downfield from those in **1**, reflecting the electron-withdrawing effect of the $M(CO)_5$ group. The individual resonances for the carbonyl carbon atoms CO_{cis} and CO_{trans} are well-resolved and distinguishable (relative intensity 4:1, respectively). An interesting feature of the ^{13}C NMR spectra of **2**−**4** concerns the detection of coupling on the $M(CO)_5$ carbons with ^{207}Pb and ^{183}W nuclei (for **4**). The values of the $^2J(^{13}C-^{207}Pb)$ coupling constants for the *transoid* CO ligands in **3** and **4** are about twice as large as those for the *cisoid* CO ligands. For unknown reasons, for the

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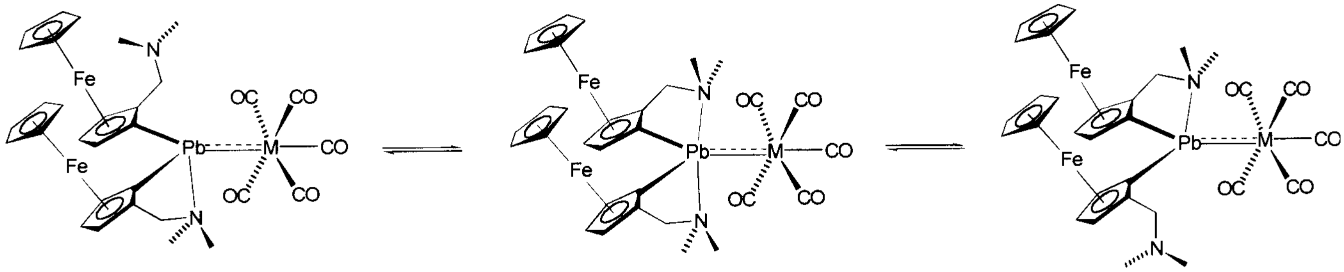
Table 2. NMR Data for Compounds 2−4 in THF-d_8

compd	$\delta_H(NMe_2)$	$\delta_H(CH_2N)$	$\delta_C(CO_{cis})$	$\delta_C(CO_{trans})$
2 (23 °C)	2.41	2.98, 4.25	220.9 ($^2J_{C,Pb} = 122$ Hz)	224.4 ($^2J_{C,Pb} = 95$ Hz)
2 (−80 °C)	2.04, 2.44, 2.59, 2.63	2.87, 3.03, 4.09, 4.45		
3 (23 °C)	2.47	3.07, 4.11	209.7 ($^2J_{C,Pb} = 82$ Hz)	212.6 ($^2J_{C,Pb} = 153$ Hz)
3 (−80 °C)	2.45, 2.50, 2.52, 2.78	3.05, 3.12, 3.94, 4.35		
4 (23 °C)	2.42	3.01, 4.04	201.3 ($^2J_{C,Pb} = 65$, $^1J_{C,W} = 125$ Hz)	200.7 ($^2J_{C,Pb} = 127$, $^1J_{C,W} = 167$ Hz)
4 (−80 °C)	2.25, 2.47, 2.58, 2.79	2.90, 3.08, 4.08, 4.45		

Scheme 2



compound **2** the coupling constant for the *transoid* CO ligand is unexpectedly small. The coupling constants increase from W to Cr in accord with a decrease of metal radii, except for a *transoid* coupling constant for **2**. The $^1J(^{13}C-^{183}W)$ coupling in **4** involving the *transoid* CO ligand (167 Hz) is larger than that of the *cisoid* CO ligands (125 Hz) and may be compared with the value of 124 Hz in $W(CO)_6$. These observations are fully in accord with our structural findings indicating stronger $W-C(CO_{trans})$ bonds.

Although the $[M(CO)_5L]$ species are often analyzed on the basis of idealized C_{4v} point-group symmetry, in the IR spectra of metalloplumbylenes **2**−**4**, severe deviations were observed. The true molecular symmetry cannot actually be higher than C_1, because when the local symmetry of the $(FcN)_2Pb$ group, which cannot be higher than C_2, is combined with the C_{4v} symmetry of the $M(CO)_5$ moiety, all symmetry elements are annihilated and all fundamentals become IR-active. Thus, the B_1 band, although IR-forbidden for rigorous C_{4v} symmetry, was assigned in the spectra of **2**−**4**,[11] in accord with the true molecular symmetry (**2**, 1967 cm^{-1}; **3**, 1986 cm^{-1}; **4**, 1969 cm^{-1}). For **2** an accidental degeneracy of the A_1'' and E_1 modes is observed (1924 cm^{-1}). These data can be correlated with those of other $M(CO)_5L$ species.[2,11] Since the unique CO_{trans} is involved in the A_1' mode, the position of this band is indicative of the π-acceptor ability of the $(FcN)_2Pb$ group. The data imply that the $(FcN)_2Pb$ ligand is a strong donor but also possesses π-acceptor strength comparable to those of R_3P ligands,[8] which is again in accord with the NMR and structural findings (vide supra).

Finally, the lack of reaction between $(FcN)_2PbM(CO)_5$ and PPh_3 in refluxing toluene is interesting in two ways. It provides another qualitative proof, besides X-ray crystallographic studies (vide supra), of a rather strong Pb−M bond and the relative donor strength of both ligands, and it is a further indication that the acceptor lead 6p orbitals are inaccessible in such complexes.

Experimental Section

General Procedures. All experiments were carried out using standard Schlenk techniques under a purified argon atmosphere. Solvents used in reactions were distilled from sodium benzophenone ketyl prior to use. The commercial products *n*-butyllithium (1.6 M solution in hexane), $PbCl_2$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $(CH_3)_3NO$, PPh_3, and (dimethylaminomethyl)ferrocene were used without further purification. The starting compounds FcNLi[12] and $Mo(CO)_5(NMe_3)$[13] were prepared according to the literature. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Infrared data were recorded on a Perkin-Elmer PE-1430 instrument.

$(FcN)_2PbCr(CO)_5$ (2). To a solution of $Cr(CO)_6$ (4.1 mmol) in THF (40 mL), irradiated by UV light for 5 h, was added **1** (2.86 g, 4.1 mmol) in THF (15 mL) at room temperature. The reaction mixture was stirred for 24 h. After the solvent was removed, the orange residue was extracted with pentane (20 mL). After filtration, the orange solution was concentrated under reduced pressure to incipient crystallization and stored at −30 °C to give **2** as orange crystals. Yield: 3.38 g, 93%. Mp: 153 °C. Anal. Calcd for $C_{31}H_{32}PbCrFe_2N_2O_5$: C, 42.14; H, 3.65; N, 3.17. Found: C, 41.7; H, 3.75; N, 3.12; H, 3.13. ^1H NMR (THF-d_8, 30 °C): δ 2.41 (s, 12 H, NMe_2), 2.98 (d, 2H, CH_2N, $J = 13$ Hz), 4.25 (d, 2H, CH_2N, $J = 13$ Hz), 4.06 (s, 10 H, Cp), 4.06 (s, 2 H, C_5H_3), 4.27 (s, 2 H, C_5H_3), 4.44 (s, 2H, C_5H_3). ^{13}C NMR (THF-d_8, 30 °C): δ 46.8 (NMe_2), 63.5 (CH_2N), 68.8 (C_5H_3), 69.4 (Cp), 97.8 ($C_5H_3-CH_2N$), 71.7 (C_5H_3), 76.9 (C_5H_3), 220.9 (CO_{cis}, $^2J_{C,Pb} = 122$ Hz), 224.4 (CO_{trans}, $^2J_{C,Pb} = 95$ Hz). IR (ν_{CO}, THF, cm^{-1}): 2044 (w), 1967 (w), 1924 (s).

$(FcN)_2PbMo(CO)_5$ (3). (a) Using a similar procedure as for **2**, $Mo(CO)_6$ (4.1 mmol) in THF (40 mL) and **1** (2.86 g, 4.1 mmol) in THF (15 mL) gave orange crystals of **3**. Yield: 3.72 g, 98%. Mp: 154 °C. Anal. Calcd for $C_{31}H_{32}PbMoFe_2N_2O_5$: C, 40.13; H, 3.45; N, 3.02. Found: C, 39.88; H, 3.69; N, 2.96. ^1H NMR (THF-d_8, 30 °C): δ 2.47 (s, 12 H, NMe_2), 3.07 (d, 2H, CH_2N, $J = 13$ Hz), 4.11 (d, 2H, CH_2N, $J = 13$ Hz), 3.89 (s, 10 H, Cp), 3.97 (s, 2 H, C_5H_3), 4.16 (s, 2 H, C_5H_3), 4.27 (s, 2 H, C_5H_3). ^{13}C NMR (THF-d_8, 30 °C): δ 46.9 (NMe_2), 63.1 (CH_2N), 69.0 (C_5H_3), 69.4 (Cp), 70.5 (C_5H_3), 76.9 (C_5H_3), 96.0 ($C_5H_3-CH_2N$), 209.7 (CO_{cis}, $^2J_{C,Pb} = 82$ Hz), 212.6 (CO_{trans}, $^2J_{C,Pb} = 153$ Hz). IR (ν_{CO}, THF, cm^{-1}): 2060 (w), 1986 (w), 1936 (s), 1916 (m).

(b) **1** (0.69 g, 1.0 mmol) in toluene (20 mL) was added to $Mo(CO)_5(NMe_3)$ (0.3 g, 1.0 mmol) in toluene (20 mL) at room temperature with constant stirring. The reaction mixture was worked up as above. Yield: 0.90 g, 97%.

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Table 3. Crystallographic Data for 2−4

	2	3	4
empirical formula	$C_{31}H_{32}PbCr$-$Fe_2N_2O_5$	$C_{31}H_{32}PbMo$-$Fe_2N_2O_5$	$C_{31}H_{32}PbW$-$Fe_2N_2O_5$
mol mass	883.48	927.42	1015.33
cryst size (mm)	0.40 × 0.30 × 0.30	0.43 × 0.27 × 0.23	0.21 × 0.13 × 0.11
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	16.3810(10)	16.453(8)	16.4730(8)
b (Å)	11.1866(6)	11.277(6)	11.2889(3)
c (Å)	16.9267(5)	16.996(8)	16.9908(8)
β (deg)	90.647(3)	90.820(10)	90.765(3)
V (Å^3)	3101.6(3)		3159.4(2)
Z	4	4	4
d_{calcd} (g cm^{-3})	1.892	1.954	2.135
T (K)	173(2)	173(2)	173(2)
μ (mm^{-1})	6.71	6.66	9.88
θ_{max} (deg)	28.29	28.58	28.33
no. of rflns	20 437	33 047	20 202
R1($I > 2\sigma(I)$)	0.0233	0.0194	0.0362
wR2(all data)	0.0457	0.0425	0.0693
goodness of fit	1.038	1.081	1.082

$(FcN)_2PbW(CO)_5$ (4). Using a similar procedure as for **2**, $W(CO)_6$ (4.1 mmol) in THF (40 mL) and **1** (2.86 g, 4.1 mmol) in THF (15 mL) gave orange crystals of **4**. Yield: 3.87 g, 93%. Mp: 153 °C. Anal. Calcd for $C_{31}H_{32}PbWFe_2N_2O_5$: C, 36.67; H, 3.18; N, 2.76. Found: C, 36.33; H, 3.21; N, 2.74. ^1H NMR (THF-d_8, 30 °C): δ 2.42 (s, 12 H, NMe_2), 3.01 (d, 2H, CH_2N, $J = 13$ Hz), 4.24 (d, 2H, CH_2N, $J = 13$ Hz), 4.10 (s, 10 H, Cp), 4.24 (s, 2 H, C_5H_3), 4.29 (s, 2 H, C_5H_3), 4.39 (s, 2 H, C_5H_3). ^{13}C NMR (THF-d_8, 30 °C): δ 47.4 (NMe_2), 62.8 (CH_2N), 69.0 (C_5H_3), 69.6 (Cp), 70.7 (C_5H_3), 76.8 (C_5H_3), 95.6 ($C_5H_3{-}CH_2N$, $^2J_{C,Pb} = 32$ Hz), 200.7 (CO_{trans}, $^2J_{C,Pb} = 127$ Hz, $^1J_{C,W} = 167$ Hz), 201.3 (CO_{cis}, $^2J_{C,Pb} = 65$ Hz, $^1J_{C,W} = 125$ Hz). IR (ν_{CO}, THF, cm^{-1}): 2060 (w), 1969 (w), 1928 (s), 1891 (m).

Reaction of $(FcN)_2PbM(CO)_5$ (M = Cr (2), Mo (3), W (4)). Adding PPh_3 (0.3 mmol, 0.065 g) to a solution of $(FcN)_2PbM(CO)_5$ (**2**−**4**; 0.3 mmol) in toluene-d_8 (10 mL), with stirring at room temperature, gave no observable reaction. Heating the reaction mixture to reflux temperature for 1 day and monitoring by ^1H NMR indicated that no reaction had occurred within this time.

X-ray Structure Analyses of 2−4. Crystal and numerical data of the structure determinations are given in Table 3. Crystals were covered with inert oil and mounted on a glass fiber and then transferred to the diffractometer in a stream of a cold gas (Siemens SMART CCD system). Monochromatic Mo Kα radiation ($\lambda = 71.073$ pm) was used. Data were corrected for Lorentz and polarization effects. Absorption correction (multiscan method SADABS) was employed. The structures were solved by direct methods using the SHELXS program and refined by full-matrix least squares against F^2 with SHELXL-97.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were treated as riding or as rigid methyl groups.

Crystallographic data (excluding structure factors) for the reported structures have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 146610−146612 (**2**−**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44-1223/336-093; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. N.S. thanks Dr. Adolphus A. H. van der Zeijden for fruitful discussions. K.J. thanks the Deutsche Forschungsgemeinschaft DFG for financial support. N.S. thanks the DFG program "Graduierten-Kolleg: Synthese und Reaktionsverhalten von Organometallverbindungen und Metallkomplexen" for a fellowship.

Supporting Information Available: Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000796A

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