chemical preparation. When 0.78 mmol of **2**·$[PF_6]$ and 8.3 mmol of 1,5-cod were stirred under nitrogen for 2 h in 2.5 mL of propylene carbonate, the solution turned from yellow-green to red-orange with precipitation of the displaced hexamethylbenzene. Addition of diethyl ether resulted in separation of a brown oil that was crystallized after adding more ether (about 80 mL in total). Filtration and twice repeated crystalization from CH_2Cl_2/ether gave 0.69 mmol (88% yield) of red-orange crystals of $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}1,5\ cod)][PF_6]$[4]. Yellow crystals of the corresponding norbornadiene complex $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}C_7H_8)][PF_6]$ have been similarly isolated,[5] and reactions with several other cyclic polyolefins, including cyclohexadiene, cycloheptadiene, cycloheptatriene and cyclooctatetraene, have been monitored electrochemically.

2 is a formally 20-electron species. However, unlike the isoelectronic $(\eta\text{-}C_6Me_6)_2Ru$, which relieves its electronic strain by having one η^4 arene,[6] it has two planar η^6-arenes.[7] Replacement of one arene by a diene thus results in the stable 18-electron complexes **1**. Apparently, a key intermediate in the ligand-exchange process is the solvento-species $(\eta^6\text{-}C_6Me_6)Co(solv)_n{}^+$, where $n = 2$ (or possibly 3).

The complexes **1** are of interest as cationic analogues of $CpCo(\eta^4$-polyolefin) complexes, which can undergo isomerizations of the polyolefin when reduced.[8] The new (hexamethylbenzene)cobalt cationic complexes are very well-behaved electrochemically, showing one-electron reductions in nonaqueous media. Their E^0 potentials are shifted by a volt or more positive of the corresponding CpCo(polyolefin) reductions, befitting the positive charge on the arene complexes. Cyclic voltammetry studies of **1** (polyolefin = 1,5-cod or norbornadiene) show that the reduction to the neutral 19-electron radical $(\eta^6\text{-}C_6Me_6)Co(\eta^4$-polyolefin) is fully reversible and diffusion controlled. In propylene carbonate at a scan rate of 100 mV/s, separation of the anodic and cathodic peak potentials is 60 mV and the anodic to cathodic current ratio is 1.0. The cathodic current function $(i_{pc}/v^{1/2})$ is constant (±1%) over an order of magnitude change in scan rate.[9]

We are currently investigating other reactions of **2** and the structure and reactions of the radicals derived from the electroreduction of **1**.

Acknowledgment. This work has been generously supported by the National Science Foundation (CHE-8303974). We thank Dr. Ulrich Koelle for helpful correspondence.

Registry No. **2**·$[PF_6]$, 53382-65-3; $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}1,5\text{-}Cod)][PF_6]$, 92694-81-0; $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}C_7C_8)][PF_6]$, 92694-83-2; $(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}1,5\text{-}Cod)$, 92694-84-3; $(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}C_7H_8)$, 92694-82-1; $(\eta^6\text{-}C_6Me_6)_2Co^{2+}$, 53382-66-4; cyclohexadiene, 29797-09-9; cycloheptadiene, 29828-02-2; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9.

---

[4] Data for $[(\eta^6\text{-}C_6Me_6)Co(1,5\text{-}cod)][PF_6]$: ^1H NMR (CD_2Cl_2) δ 3.19 (br s, 4 H), 2.51 (m, 4 H), 2.18 (s, 18 H), 1.80 (m, 4 H). Calcd for $C_{20}H_{30}CoPF_6$: C, 50.64; H, 6.38. Found: C, 50.48; H, 6.52.

[5] Data for $[(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}C_7H_8)][PF_6]$: ^1H NMR (CD_2Cl_2) δ 3.36 (m, 2 H), 2.97 (dd, 4 H), 2.24 (s, 18 H), 1.03 (t, 2 H). Calcd for $C_{19}H_{26}CoPF_6$: C, 49.79; H, 5.72. Found C, 49.50; H, 5.87.

[6] (a) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* **1970**, *103*, 162. (b) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2049.

[7] Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979.

[8] (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1983**, *105*, 1772.

[9] The significance of these observations is as follows. The 60-mV peak separation (independent of scan rate) is consistent with an electrochemically reversible (fast electron transfer) one-electron process. The value of unity for the current ratio shows that the electrode product (the neutral radical) is stable over the cyclic voltammetry time scale (ca. 10 s here), and the constant current function (peak cathodic current divided by square root of scan rate) is indicative of a diffusion-controlled process.

Thermolysis Reactions of Iron and Ruthenium Metallocarboxylic Acids

Dorothy H. Gibson* and Tek-Sing Ong

Department of Chemistry, University of Louisville
Louisville, Kentucky 40292

Received June 21, 1984

Summary: A new synthesis of $CpFe(CO)(PPh_3)COOH$ is described as is the preparation of a new metallocarboxylic acid, $CpRu(CO)(PPh_3)COOH$. Upon heating, the iron acid provided $Cp_2Fe_2(CO)_3(PPh_3)$, as the first isolable product, which resulted from reaction of the acid with its decarboxylation product $CpFe(CO)(PPh_3)H$. The ruthenium acid decarboxylated to the hydride in acetone, but it was stable to thermolysis in benzene. The ruthenium acid is not reactive toward $CpM(CO)(PPh_3)H$ (M = Fe, Ru). Thermolyses in chlorinated solvents take place wholly (iron acid) or in part (ruthenium acid) by redox paths; both acids were also readily oxidized by Ag^+.

Studies of metallocarboxylic acids are of interest because of the proposed intermediacy of such complexes in metal carbonyl catalyzed water gas shift reactions.[1] Although relatively few metallocarboxylic acids have been isolated and studied thoroughly,[2] one of the reactions that has been thought to be characteristic of this class of compounds is decarboxylation, induced by heating and, in some instances, catalyzed by base.

A preliminary account of the preparation of $CpFe(CO)(PPh_3)COOH$ (**1a**) and several of its derivatives appeared several years ago.[2c] The thermal instability was noted, but, although decarboxylation was suggested, the thermolysis products were not identified. As part of a general study of metallocarboxylic acids,[2e,j] we have prepared **1a** and its ruthenium analogue **1b** and studied the thermolysis reactions of these two acids.

$CpM(CO)(PPh_3)COOH$
1a, M = Fe
1b, M = Ru

$CpM(CO)_2(PPh_3)^+X^-$
2a, M = Fe, X = BF_4
2b, M = Ru, X = BF_4
2c, M = Fe, X = Cl
2d, M = Ru, X = Cl

$CpM(CO)(PPh_3)X$
3a, M = Fe, X = H
3b, M = Ru, X = H
3c, M = Fe, X = Cl
3d, M = Ru, X = Cl

---

[1] Pettit, R.; Mauldin, C.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 151. (b) For a recent review of the WGS reaction see: Ford, P. C. *Acc. Chem. Res.* 1981, *14*, 31.

[2] Although widely invoked as probable intermediates in reactions involving OH^- and metal carbonyls, few examples of these complexes have been observed: (a) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 443. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *103*, 741 [see also: Sweet, J. R.; Graham, W. A. G. *Organometallics* 1982, *1*, 982. (c) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *103*, 1627. (d) Catellini, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566. (e) Gibson, D. H.; Hsu, W.-L.; Ahmed, F. U. *J. Organomet. Chem.* **1981**, *215*, 379. (f) Tam, W.; Lin, G.-Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (g) Alton, J. G.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1983**, *246*, C23. (h) Barrientos-Penna, C. F.; Gilchrist, A. B.; Sutton, D. *Organometallics* **1983**, *2*, 1265. (i) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88. (j) Gibson, D. H.; Owens, K.; Ong, T.-S. *J. Am. Chem. Soc.* **1984**, *106*, 1125.

0276-7333/84/2303-1911$01.50/0

The synthetic method we have employed differs from the one described earlier for **1a** and provides better yields of both acids than we were able to achieve by the previous method.[2c] For **1a**, CpFe(CO)$_2$(PPh$_3$)$^+$BF$_4^-$ (**2a**)[3] was dissolved in CH$_2$Cl$_2$ and cooled to −60 °C; an equivalent of Et$_4$NOH (in methanol) was then added, and this mixture was maintained at −60 °C for 10 min. After this time, the mixture was warmed to 0 °C during about 15 min; an IR spectrum of the reaction mixture indicated that the cation had reacted completely and bands for **1a** were visible. The mixture was filtered while it was still cold, and solvent was removed from the filtrate on a rotary evaporator; the residue was then triturated with several small portions of CH$_2$Cl$_2$/pentane, and these were concentrated to a small volume and then cooled to −30 °C, affording the acid[5] in 63% yield as a yellow powder: mp 128–130 °C (lit.[2c] mp 130 °C dec); IR (Nujol) 1930 (s), 1565 (m, br) cm^{-1} [lit.[2c] (Nujol) 1930, 1565 cm^{-1}]. Reaction of CpRu(CO)$_2$(PPh$_3$)$^+$BF$_4^-$ (**2b**)[6] in similar manner at 0 °C for 5 min, followed by a similar workup provides **1b** in 85% yield.[9]

On the basis of the behavior of other systems,[2] decarboxylation of a metallocarboxylic acid is expected to lead to the corresponding metal hydride; therefore the expected decarboxylation product of **1a** is **3a**. Previous work[2c] with **1a** indicated that decomposition, with CO$_2$ loss, occurred upon warming it in benzene solution; thus our first thermolysis reaction of **1a** was conducted in that solvent.

A sample of **1a** was placed in an NMR tube with benzene-d_6 and heated slowly to 65 °C; its ^{1}H NMR spectrum was recorded, periodically, over a period of 14 h. After this time, the sample consisted of approximately equal proportions of the starting compound together with [CpFe(CO)$_2$]$_2$ (**4**). Since the reaction in benzene required a long time for completion, we selected another solvent in hopes that milder conditions could be found that might allow the observation of **3a**.

Thermolysis of **1a** in acetone-d_6 at 50 °C was complete after 1 h and afforded dimer **4** as the only organometallic product; however, a green color was evident in the solution until the final stages of the thermolysis. When the thermolysis was conducted at 40 °C in acetone-d_6, the reaction mixture became deep green and a third compound was evident in NMR spectra recorded after a few minutes at this temperature. After 2 h at 40 °C, a ^{1}H NMR spectrum showed cyclopentadienyl resonances at δ 4.61, 4.30, and 4.95 with the first two being equal in intensity and predominant; the low-field peak corresponded to the dimer **4**. An IR spectrum of a sample of this mixture in hexane revealed bands at 1960 (s), 1937 (m), and 1740 (s) cm^{-1} in addition to bands for the dimer. Comparison of the IR and NMR spectral bands of this new component with those from an authentic sample of Cp$_2$Fe$_2$(CO)$_3$(PPh$_3$) (**5**)[10] showed that the two were identical. On a preparative scale, compounds **4** and **5** were formed in 9% and 69% yields, respectively, from thermolysis of the metallocarboxylic acid in acetone at 40 °C. Dimer **5** was converted to **4** upon further heating in acetone. The expected decarboxylation product CpFe(CO)(PPh$_3$)H (**3a**) was not observed in any of the thermolysis reactions although a sample of **3a**[11] was stable under the conditions of the thermolysis experiment in acetone; thus **5** did not result from disproportionation of **3a**.

Several possible paths for the formation of dimer **5** occurred to us, two of which involve acid **1a** as a reactant: (a) CpFe(CO)$_2$H (**6**)[12] with **1a** and (b) CpFe(CO)(PPh$_3$)H with **1a**. Mixing equimolar quantities of **6** with **1a** in benzene solution at room temperature leads to dimer **4**; reaction was complete after 4 h. A control sample of the hydride, in benzene, was allowed to stand at room temperature until conversion to the dimer was complete; the conversion required about 12 h. A similar experiment with **3a** and **1a** resulted in slow formation of dimer **5** (a small amount of the dimer was evidenced after 3 h at room temperature). In acetone at room temperature, equimolar quantities of **3a** and **1a** afforded dimer **5** only; reaction appeared to be complete after 30 min. Since it also seemed possible that **5** might be formed from CpFe(CO)$_2$(PPh$_3$)$^+$ (generated by ionization of **1a**) and hydride **3a**, we mixed equimolar quantities of **2a** and **3a** in acetone at 40 °C also. Neither dimer **4** nor **5** was formed. Thus it appears that a direct reaction between metallocarboxylic acid **1a** and its decarboxylation product **3a** is responsible for the formation of **5**. Slow addition of the solid acid **1a** to acetone at 40 °C also leads exclusively to **5**, and thus the high reactivity of the hydride **3a** toward the acid prevents complete decarboxylation of **1a**. Reactions between metal hydrides and a metallocarboxylic acid have not been reported previously.

The thermolysis behavior of the ruthenium complex **1b** in benzene and acetone is completely different than that of its iron analogue. Compound **1b** showed no evidence of decomposition after 3 days at 70 °C in benzene whereas it completely decarboxylated to the hydride **3b** after 2 h in acetone at 50 °C. No dimer such as **4** or **5** was observed; also **1b** does not react with hydride **3a** and **1a** does not react with hydride **3b**. Thus the activity of the hydride as well as the lability of the hydroxyl group in the metallocarboxylic acid appear to influence the reactivity of these compounds.

In order to probe the reaction characteristics of **1a** and **1b** further, we have also examined the thermolyses of the two acids in chlorinated solvents. At room temperature in CCl$_4$, **1a** was converted to CpFe(CO)$_2$(PPh$_3$)$^+$Cl$^-$ (**2c**)[4] in 89% yield after 5 h. Reaction of **1a** with CDCl$_3$ was slower, requiring 3 days at room temperature for complete reaction to occur, but the result was the same. In neither case was CpFe(CO)(PPh$_3$)Cl (**3c**),[11] the product expected from decarboxylation followed by reaction of the hydride with solvent, seen as a product. Conversion of CpFe(CO)$_2$Cl and PPh$_3$ to **2c** does take place slowly; the rate is not comparable to the rate of conversion of **1a**.

At 50 °C in CDCl$_3$, ruthenium compound **1b** required 2 days for complete conversion to products; CpRu(CO)$_2$-

---

[3] Prepared by reaction of **2c**[4] with AgBF$_4$; IR ν_{CO} (CH$_2$Cl$_2$) 2053 and 2013 cm^{-1} (PF$_6$ salt: 2055 and 2010 cm^{-1} Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177).

[4] Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172.

[5] Anal. Calcd for C$_{25}$H$_{21}$O$_3$PFe: C, 65.81; H, 4.64; P, 6.79. Found: C, 65.57; H, 4.79; P, 6.50. ^{1}H NMR (acetone-d_6): δ 4.51 (s) and 7.40 (m) with relative areas 5:15, respectively. ^{13}C NMR (CD$_2$Cl$_2$): δ 84.62 (s), 128.00 (d, 9.6 Hz), 129.83 (s), 133.14 (d, 9.7 Hz), 135.89 (d, 44.0 Hz), 214.30 (d, 34.6 Hz), and 220.00 (d, 30.4 Hz).

[6] Prepared by reaction of **2d**[7] with AgBF$_4$; its properties were identical with those reported by Humphries and Knox.[8]

[7] Jungbauer, A.; Behrens, H., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1083.

[8] Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans* **1975**, 1710.

[9] IR ν_{CO} (Nujol): 1936 (s) and 1593 (m) cm^{-1} (mp 119–121 °C dec). ^{1}H NMR (acetone-d_6): δ 5.01 (s) and 7.55 (m) with relative areas 5:15, respectively. ^{13}C NMR (CD$_2$Cl$_2$): δ 87.66 (s), 127.59 (d, 9.7 Hz), 129.60 (s), 132.92 (d, 10.3 Hz), 135.33 (d, 48.9 Hz), 199.00 (d, 19.2 Hz), and 204.36 (d, 18.3 Hz).

[10] Haines, R. J.; duPreez, A. L. *Inorg. Chem.* **1969**, *8*, 1459.

[11] Kalck, P.; Poilblanc, R.; Gallais, M. F. *C. R. Hebd. Seances Acad. Sci.* **1972**, *274*, 66.

[12] A sample of compound **6** was prepared by borohydride reduction of CpFe(CO)$_2$Cl; its spectral properties were identical with those described previously (Davidson, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133).

$(PPh_3)^+Cl^-$ and $CpRu(CO)(PPh_3)Cl$[13] were formed as the only products in a ratio of 1:2, respectively (determined in CD_3NO_2 solution after completion of reaction). The ionic chloride **2d** showed no conversion to the covalent chloride **3d** under these conditions, but hydride **3b** was rapidly converted to this product after brief exposure to $CDCl_3$ at 50 °C. Thus two reaction paths are available to this acid: (a) decarboxylation followed by reaction of the hydride with the solvent or (b) direct reaction with the solvent.

The ionic products formed in the reactions conducted in chlorinated solvents result from redox processes. The ease of oxidation of both acids is evidenced by their rapid conversion to the corresponding cations $CpM(CO)_2(PPh_3)^+$ (M = Fe, Ru), by treatment with a catalytic amount of $AgBF_4$.[14] Thus, the reactions of **1a,b** appear to parallel the behavior of $CpFe(CO)(PPh_3)CH_3$ and related complexes in the presence of oxidizing agents; such alkyl complexes are converted to cation radicals by the action of catalytic amounts of $AgBF_4$ or $Ph_3C^+BF_4^-$.[15,16] Since cation radicals formed from organic carboxylic acids in mass spectrometers fragment in part by loss of ·OH to leave an acylium ion,[17] a similar fragmentation path may be expected for cation radicals formed from metallocarboxylic acids. The single product resulting from reactions of the iron acid with chlorinated solvents presumably reflects a lower ionization potential for **1a** in comparison to **1b** as expected.[18]

Work is in progress to establish other reaction characteristics of these two metallocarboxylic acids.

Acknowledgment. We are grateful to The Academic Excellence Commission, the Graduate Research Council, and the Arts and Sciences Research Committee of the University of Louisville for support of this work.

Registry No. **1a**, 70196-11-1; **1b**, 92670-59-2; **2a**, 32614-25-8; **2b**, 57327-09-0; **2c**, 12100-38-8; **2d**, 92670-60-5; **3a**, 32660-22-3; **3b**, 57327-06-7; **3d**, 32613-25-5; **4**, 12154-95-9; **5**, 60909-85-5; **6**, 35913-82-7; $CpFe(CO)_2Cl$, 12107-04-9.

---

[13] Identified by spectral comparison with an authentic sample (Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376).

[14] Although strong acids promote ionization of both **1a** and **1b**, stoichiometric quantities are needed to effect complete ionization. Also, **1a** and **1b** do not ionize upon standing in acetone solution for short periods of time although more polar solvents do cause ionization (see ref 2c).

[15] (a) Magnuson, R. W.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (b) Magnuson, R. W.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460.

[16] Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, *3*, 642.

[17] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; 4th ed.; Wiley: New York, 1981; Chapter 2.

[18] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 17.

Synthesis and Structure of a Bimetallic Iron Carbonyl–Diazadiphosphetidine Complex, $Fe_2(CO)_8[P_2(t\text{-}BuN)_2(H)_2]$

Donn A. DuBois, Eileen N. Duesler, and Robert T. Paine*

Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

Received July 24, 1984

Summary: The reaction of $Na_2Fe(CO)_4{\cdot}{}^3/_2$dioxane with cyclic ClPN(*t*-Bu)P(Cl)N(*t*-Bu) in a 1:2 ratio in THF or Et_2O results in the formation of $Fe(CO)_4$[(H)PN(*t*-Bu)(P(H)N(*t*-Bu)]$Fe(CO)_4$. The structure of this unexpected complex has been determined by X-ray diffraction techniques and found to contain the previously unknown cyclic four-membered diazadiphosphetidine ring (H)PN(*t*-Bu)P(H)N(*t*-Bu) with each phosphorus atom bonded to a $Fe(CO)_4$ fragment.

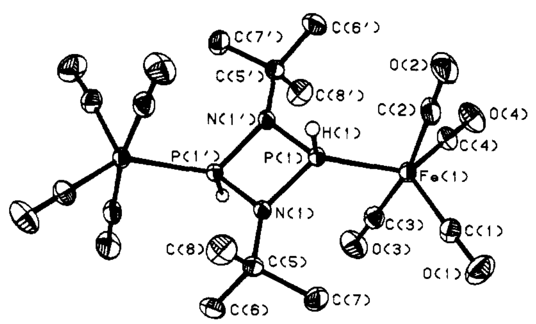

Figure 1. Molecular geometry and atom labeling scheme for $Fe_2(CO)_8$[(H)PN(*t*-Bu)P(H)N(*t*-Bu)].

The dihalodiphosphine 2,4-dichloro-1,3-di-*tert*-butyldiazadiphosphetidine, ClPN(*t*-Bu)P(Cl)N(*t*-Bu) (**1**), has recently been observed to undergo heterolytic P–Cl bond cleavage reactions promoted by $AlCl_3$[1,2] and $NaCp^*Mo(CO)_3$.[3,4] In the former case, a monocationic salt [ClPN(*t*-Bu)PN(*t*-Bu)$^+$][$AlCl_4^-$] (**2**) was reported. In the latter combination a monometallic complex,[5] $Cp^*Mo(CO)_2$[PN(*t*-Bu)P(Cl)N(*t*-Bu)] (**3**), and a bimetallic complex,[4] $[Cp^*Mo(CO)_2]_2$[PN(*t*-Bu)PN(*t*-Bu)] (**4**), were isolated in high yield, and the structure of **4** was determined by single-crystal X-ray diffraction methods. The P_2N_2-$(t\text{-}Bu)_2$ ring in **4** is planar, and a $Cp^*Mo(CO)_2$ fragment is bonded to each phosphorus atom with the Mo atoms residing in the P_2N_2 plane. The Mo–P bond distance 2.246 (1) Å is short, and the average P–N bond distance 1.716 (3) Å is long compared to the distance found in **1**, 1.689 (4) Å.[6] On the basis of this structure we suggested that there exist formal Mo═P multiple bond interactions comprised of P lone pair → Mo dz^2 donation and Mo $d_{xz} \rightarrow p\ \pi^*$ back-donation.[7] The ligand **1** has subsequently revealed new, more complex chemistry with several other transition-metal fragments.[8] We report here on the interaction of $Na_2Fe(CO)_4{\cdot}{}^3/_2$dioxane[9] with **1** in a 1:2 ratio

---

[1] Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.

[2] Light, R. W. Ph.D. Thesis, University of New Mexico, 1979.

[3] Abbreviations used in the text include Cp* = $(CH_3)_5C_5$, THF = tetrahydrofuran, and Et_2O = diethyl ether.

[4] DuBois, D. A.; Duesler, E. N.; Paine, R. T. *Organometallics* **1983**, *2*, 1903.

[5] The monometallic complex **3** and the corresponding complex containing a C_5H_5 ligand in place of the Cp* ligand have been prepared and will be described in a subsequent paper. Light, R. W. Ph.D. Thesis, University of New Mexico, 1979.

[6] Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259.

[7] The nature of the bonding interactions is closely related to that previously described for $Cp^*Mo(CO)_2\ PN(CH_3)CH_2CH_2NCH_3$: Hutchins, L. D.; Campana, C. F.; Paine, R. T. *J. Am. Chem. Soc.* **1980**, *102*, 4521.

[8] DuBois, D. A.; Duesler, E. N.; Paine, R. T., manuscripts in preparation.

[9] Commercially available from Alpha Products, Thiokol, Ventron Division.