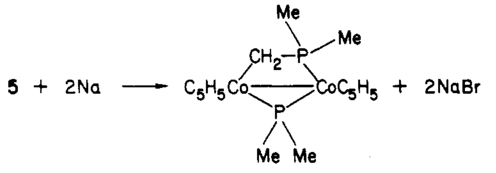
the cobalt atoms. The small difference between the distances P(1)–C(1) and P(1)–C(2), P(1)–C(3) indicates that the P–C bond of the PMe_2–CH_2 bridge probably has no double-bond character. This contrasts with the situation in the related compound $[(PMe_3)_4Co_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)]$ for which the CH_2–P distance (1.707 (10) Å) is significantly shorter than the P–CH_3 distances (average 1.83 Å).[13]

The synthesis of the binuclear complex **6** could also be achieved. Whereas oxidative addition of CH_2Br_2 to **1** leads to cleavage of the metal–metal bond, reduction of **5** with Na–Hg reforms this Co–Co bond.[14] Although the dark brown crystals of **6** obtained from the pentane solution at −78 °C are disordered in the PMe_2 and CH_2PMe_2 bridges, the Co–Co distance of 2.565 (2) Å is nearly identical with that in **1**.



(3)

6

In conclusion, it has now been proved that it is possible to transform a M–PMe_2–M into a M–CH_2–PMe_2–M unit in two steps by using a dihalomethane as the CH_2 source. During this process, the remaining coordination sphere of the metal atoms is unchanged. This result deserves comment. Most recently it has been found by Wojcicki et al. that the dianions $[(NO)_2Fe(\mu\text{-}NO)(\mu\text{-}PPh_2)Fe(NO)PPh_2]^{2-}$ and $[(CO)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_2PPh_2]^{2-}$ react with CH_2I_2 to produce $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)Fe(NO)_2]$ and $[(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)Fe(CO)_3]$, respectively.[15] Whereas in these reactions nucleophilic substitution of the two halides of CH_2I_2 occurs, in the formation of **4** and **5** from **1** and CH_2X_2 no atom or ion is eliminated; i.e., a simultaneous addition to and insertion of the three fragments CH_2, X, and X into the M–PR_2–M unit takes place. There is precedent for this insofar as both Balch[16] and Schmidbaur[17] reported that the metal–metal bonded compounds $Pd_2(dppm)_3$ (dppm = bis(diphenylphosphino)methane) and $Au_2(dmpd)_2$ (dmpd = (dimethylphosphonio)dimethanide) react with CH_2X_2 to form A-frame type complexes by addition of the two halides to the two metal atoms and formation of a M–CH_2–M bridge. With regard to the reaction of **1** with CH_2X_2, the surprising fact is that the bridging phosphido ligands are less inert than generally assumed, a result for which recent evidence has also been provided by independent work from our laboratory[3c] and by other groups.[15,18]

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and structure factors for **5** (30 pages). Ordering information is given on any current masthead page.

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(13) Klein, H.-F.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1391.

(14) **5** (180 mg, 0.3 mmol) was suspended in 6 mL of ether, and Na/Hg (3%, 16 mg of Na, 0.7 mmol) was added. The solution was stirred at 25 °C for 3 h and filtered, and the solvent was removed in vacuo. The dark residue was dissolved in 5 mL of C_6H_6, and the solution was chromatographed on Al_2O_3 (Woelm, neutral, activity grade V). After removal of the solvent, the residue was dissolved in 6 mL of pentane, and the solution was cooled at −78 °C. Dark brown crystals were obtained, mp 248 °C (yield 120 mg, 94%).

(15) (a) Yu, Y.-F.; Chau, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3704. (b) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Chem. Soc., Chem. Commun.* **1984**, *653*.

(16) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M., Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

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Isomeric Zwitterions and Ferrocenophanes from the Reaction of 1-Lithio-1′-(diphenylphosphino)ferrocene with Group 6 Carbonyls

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Summary: The reaction of $Fe(C_5H_4Li\text{-}\eta^5)(C_5H_4PPh_2\text{-}\eta^5)$ with $M(CO)_6$ (M = Cr, W) followed by Me_3BF_4 affords the zwitterions $Fe(C_5H_4M(CO)_5{}^-\text{-}\eta^5)(C_5H_4PPh_2Me^+\text{-}\eta^5)$ (**3**) and the carbene-bonded ferrocenophanes $Fe(C_5H_4C(OMe)\text{-}\eta^5)(C_5H_4PPh_2M(CO)_4\text{-}\eta^5)$ (**4**). The crystal structures of **3** (M = Cr) and **4** (M = W) are described.

The ring opening reaction of the [1]ferrocenophane **1** is a convenient route to the useful lithio species **2**.[1,2] We now describe the reaction of **2** with $M(CO)_6$ (M = Cr, W) which affords two novel isomeric species, the zwitterion **3** and the carbene-based [3]ferrocenophane **4** (Scheme I). There appear to be no precedents for **3**,[3] and ferrocenophanes with transition-metal atoms in the bridge have only recently been described.[2b,4] **4** can be regarded as a derivative of an unusual bidentate hybrid ligand containing carbene and phosphine donor groups.[4,5]

The stirred orange solution of **2** produced by the reaction of **1** with 1.5 mol equiv of PhLi was treated with excess $M(CO)_6$ at −78 °C. A dark red suspension formed when the mixture was warmed to 20 °C. This was cooled to −78 °C, Me_3OBF_4 added (1.5 mol), and the mixture finally warmed to 20 °C for 2 h. Two major products, orange **3** (10–20%) and deep red **4** (20–40%), were isolated as air-stable solids following chromatography on alumina.[7]

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(1) Seyferth, D. M.; Withers, H. P. *Organometallics* **1982**, *1*, 1275.

(2) (a) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1983**, *61*, 147. (b) Butler, I. R.; Cullen, W. R. *Organometallics* **1984**, *3*, 1846. (c) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics*, in press.

(3) Cullen, W. R.; Woollins, J. D. *Coord. Chem. Rev.* **1982**, *39*, 1.

(4) There are a number of metal derivatives of ligands such as $Fe(C_5H_4PPh_2\text{-}\eta^5)_2$ which can be considered as [3]ferrocenophanes.[3]

(5) A few simple Fischer-type carbene complexes of metallocenes are known.[3,6]

(6) Fischer, E. O.; Gammel, F. J.; Besinhard, J. O.; Frank, A.; Neugebauer, D. J. *J. Organomet. Chem.* **1980**, *191*, 261.

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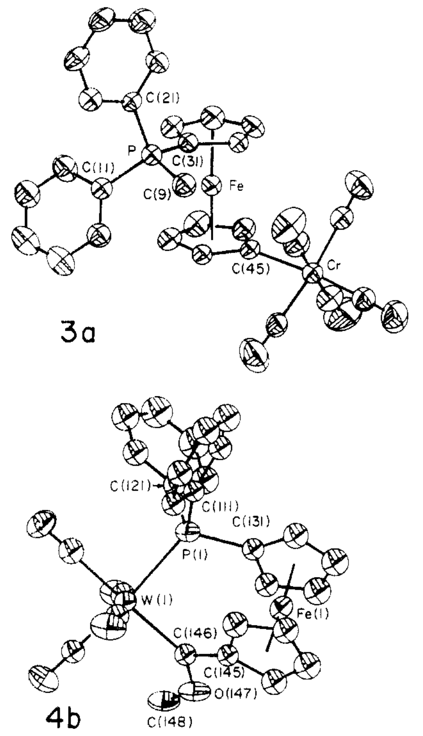
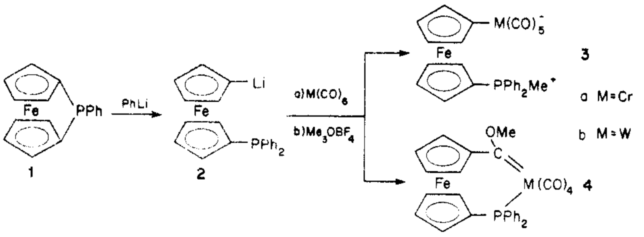


3a

4b

Figure 1. Views of **3a** and one molecule of **4b**. Thermal ellipsoids enclose 50% probabilities. Hydrogen atoms have been deleted for clarity.

Scheme I



X-ray structures were determined for **3a** and **4b**.[8] Views of **3a** and one of the three crystallographically independent molecules of **4b** are shown in Figure 1.[9] The three molecules of **4b** are structurally similar. Selected distances (Å) for **3a**:[10] Cr–C(45) = 2.149 (5); Cr–C(carbonyls cis to C(45)) = 1.872 (8) (average); Cr–C(carbonyl trans to C(45)) = 1.843 (6); P–C(9) = 1.788 (5); P–C(phenyl) = 1.796 (5) (average); P–C(31) = 1.769 (5). Averaged[9] distances (Å) and angles (deg) for **4b**: W–P = 2.550 (6); W–C(n46) = 2.199 (14); W–C(carbonyl) = 2.017 (23); P–C(phenyl) = 1.839 (14); P–C(n31) = 1.825 (25); C(n45)–C(n46) = 1.49 (2); C(n46)–O(n47) = 1.32(2); O(n47)–C(n48) = 1.44 (2); P–W–C(n46) = 90.7(4); C(n45)–C(n46)–O(n47) = 105.1 (12). The W-carbene carbon and carbene–C_5H_4 distances are both in their normal ranges.[3,6,11] The P–C distances are shorter in **3a** than in **4b**.

In view of the result that $Fe(C_5H_5)(C_5H_4PPh_2)$ does not react easily with $M(CO)_6$ at ambient temperature, it is probable that cyclization to give **4** is assisted by formation of the initial acylato complex or a later produced unidentate methyl carbene derivative. The acylato complex is probably the source of **3** via a competitive reaction of the uncomplexed–PPh_2 function with Me_3OBF_4.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial assistance.

Supplementary Material Available: Fully labeled thermal ellipsoid diagrams of **3a** and **4b** (Figures 2 and 3) and views of all three independent molecules of **4b** (Figure 4) along with details of structure refinement, tables of crystals data, data collection, positional and thermal parameters, and bond distances and angles, and structure factor listings (92 pages). Ordering information is given on any current masthead page.

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[7] Microanalytical and spectroscopic data for all four compounds are as expected. **4b**: ^{13}C NMR 311 ppm (carbene carbon).

[8] Crystals of **3a** are monoclinic of space group $P2_1/n$ with $a = 10.809$ (2) Å, $b = 10.327$ (3) Å, $c = 22.830$ (5) Å, $\beta = 90.62$ (2)°, $V = 2548.2$ Å^3, $Z = 4$; present $R_F = 0.039$ from 2301 observables. Crystals of **4b** are triclinic of space group $P\bar{1}$ with $a = 12.259$ (3) Å, $b = 14.459$ (4) Å, $c = 23.108$ (4) Å, $\alpha = 81.19$ (2)°, $\beta = 75.26$ (2)°, $\gamma = 78.86$ (2)°, $V = 3863.1$ Å^3, $Z = 6$; present $R_F = 0.045$ from 6128 observables. Data were collected by ω–2θ scans on an Enraf-Nonius CAD4F diffractometer, Mo Kα radiation (graphite monochromator) with $2\theta_{max} = 45°$ for **3a** and 40° for **4b**.

[9] Davies, E. K. "CHEMGRAF User Guide"; Chemical Crystallography Laboratory: University of Oxford, 1981.

[10] The esd's quoted with the averages were calculated by the equation $\sigma = [\sum_m (x_m - x_0)^2/(m - 1)]^{1/2}$ where $x_0 = (\sum_m x_m)/m$. When this number is less than the esd in the individual measurements, the largest $\sigma(x_m)$ is quoted.

[11] (a) Daran, J. C.; Jeannin, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1392. (b) Casey C. P.; Burkhardt, J. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

Remarkable Phase-Transfer-Catalyzed Reactions Involving Sulfur

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Summary: An unusual reaction occurs when bromo(pentacarbonyl)manganese is treated with 5 N NaOH, methylene chloride, or 4-methyl-2-pentanone as the organic phase, benzyltriethylammonium chloride as the phase-transfer agent, and elemental sulfur. An X-ray analysis of $[PhCH_2N(C_2H_5)_3{}^+]_2[(Mn(CO)_3(SCS_3))_2]^{2-}$ confirmed the presence of a perthiocarbonate ligand. Crystal data: triclinic, space group $P\bar{1}$, $a = 9.128$ (9) Å, $b = 9.720$ (12) Å, $c = 13.308$ (6) Å, $V = 1050.8$ Å^3, and $Z = 2$.

Phase-transfer catalysis is a valuable method for the synthesis of organometallic complexes and for the use of metal compounds as catalysts for a variety of reactions.[1] Recently, the first examples of the phase-transfer-catalyzed desulfurization of organic compounds were described, whereby benzylic mercaptans are converted to hydrocarbons using stoichiometric quantities of triiron dodecacarbonyl.[2] The fate of the sulfur in this reaction was not determined.

$$R_1R_2R_3CSH + Fe_3(CO)_{12} \xrightarrow[60\ °C,\ (C_4H_9)_4N^+HSO_4^-]{5\ N\ NaOH,\ C_6H_6} R_1R_2R_3CH$$

Some interesting complexes have been isolated from the reaction of sulfur with organometallic reagents under ho-

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[1] Alper, H. *Fundam. Res. Homogenous Catal.* **1984**, *4*, 79; *Adv. Organomet. Chem.* **1981**, *19*, 183.

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