Organometallics 1985, *4*, 601–603

Table III. Angles (deg) in Complexes **15a** and **15b** of $[(CpCo(\mu_2\text{-}P(Ph)(CH_2)_3P(Ph))CoCp)(\mu\text{-}H)]BF_4$

atoms	**15a**	**15b**
P1–Co1–P2	78.87 (13)	79.22 (13)
P1–Co2–P2	79.46 (13)	79.50 (13)
Co1–P1–Co2	71.62 (11)	71.68 (11)
Co1–P2–Co2	71.51 (11)	71.70 (11)
P1–Co1–Co2	53.46 (13)	54.00 (12)
P1–Co2–Co1	54.25 (12)	54.33 (13)
P2–Co1–Co2	54.74 (13)	54.07 (12)
P2–Co2–Co1	54.94 (13)	54.21 (12)
CP1–Co1–P1	134.5 (3)	135.5 (4)
CP1–Co1–P2	136.9 (3)	135.5 (4)
CP2–Co2–P1	135.9 (3)	133.6 (9), 134.1 (10)[b]
CP2–Co2–P2	134.7 (3)	135.9 (6), 138 (2)
CP1–Co1–Co2[a]	161.3 (3)	161.9 (6)
CP2–Co2–Co1[a]	161.4 (3)	163.1 (7), 160 (1)
CP1–Co1–HB1	125 (4)	119.5 (5)
CP2–Co2–HB1	119 (4)	126 (4), 124 (4)
P1–Co1–HB1	78 (4)	82 (4)
P2–Co1–HB1	82 (4)	86 (4)
P1–Co2–HB1	83 (4)	79 (4)
P2–Co2–HB1	87 (4)	82 (3)
Co1–Co2–HB1	42 (4)	37 (4)
Co2–Co1–HB1	37 (4)	42 (4)

[a] CP1 is the center of cyclopentadienyl ring 1, and CP2 is the center of cyclopentadienyl ring 2. [b] Two values for the disordered cyclopentadienyl ring with contributions A and B, respectively.

tance, 1.63 (13) Å, is consistent with the distance, 1.72 (1) Å, for the average bridging Co–H–Co distance found in a number of dicobalt complexes.[14c] The average Co–H–Co angle, 100 (6)°, is consistent with a closed two-electron, three-center bond.[14] Bonded and selected nonbonded distances for **15a** and **15b** are summarized in Table II, and the important angles are given in Table III.

Complexes **1**–**5** appear to react similarly with an excess of the electrophilic reagents H^+ and SO_2; i.e., the linked phosphido complexes are not differentiated from the unlinked cases. However, in competition experiments in which 1 equiv of H^+ is partitioned between an equimolar mixture of two different dicobalt complexes, the chelated phoshido complexes **4** and **5** appear to be more nucleophilic than the nonchelated analogue **3**.[20] These reactivity differences are being studied further.

Acknowledgment. Technical advice on the X-ray determination was provided by Dr. Judith C. Gallucci of the OSU Crystallographic Service. We are grateful to the NSF for partial support via the OSU Materials Research Laboratory and to Professor L. Dahl for providing information on the structures of **16**, **17**, and **18**.

Registry No. **1**, 66415-82-5; **2**, 94325-11-8; **3**, 94325-12-9; **4**, 94325-13-0; **5**, 94325-14-1; **6**, 94347-90-7; **7**, 94347-91-8; **8**, 94347-92-9; **9**, 94347-93-0; **10**, 94347-94-1; **11**, 94325-16-3; **12**, 94325-18-5; **13**, 94325-20-9; **14**, 94325-22-1; **15**, 94325-24-3; $(\eta^5\text{-}C_5H_5)_2Co$, 1277-43-6; $H(Ph)P(CH_2)_2P(Ph)H$, 18899-64-4; $H(Ph)P(CH_2)_3P(Ph)H$, 28240-66-6; $HP(Ph)_2$, 829-85-6; $HP(Et)_2$, 627-49-6; $HP(Me)Ph$, 6372-48-1; SO_2, 7446-09-5.

Supplementary Material Available: Tables of analytical data, fractional coordinates of atoms, thermal parameters, hydrogen positional parameters, and observed and calculated structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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[20] Presented in part at the: 188th National Meeting of American Chemical Society, Philadelphia, PA, Aug 1984; American Chemical Society: Washington, DC, 1984; INORG, 274.

Novel Dinuclear CH_2PMe_2-Bridged Cobalt Complexes by Simultaneous Three-Fragment Oxidative Addition and Insertion Using Dihalomethanes as Substrates[1]

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Summary: $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (**1**) reacts with CH_2I_2 and CH_2Br_2 to form the complexes $[C_5H_5(X)Co(\mu\text{-}PMe_2)]_2$ (**2**, **3**) and $[(C_5H_5)_2(X)_2Co_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)]$ (**4**, **5**), respectively. **2** and **3** are also prepared from **1** and equimolar amounts of X_2 (X = I, Br). Reduction of **5** with Na–Hg gives the compound $[(C_5H_5)_2Co_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)]$ (**6**) which according to X-ray data contains a metal–metal bond. The crystal structure of **5** (trans isomer) has been determined.

Recently, we observed that the feature of metal basicity known for various cyclopentadienylcobalt and -rhodium compounds[2] is not confined to species having only *one* metal center. The binuclear complexes $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ and $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$, in which the two metal atoms are coordinated *formally* in a similar way to those in the compounds $C_5R_5M(PMe_3)_2$ (M = Co, Rh), react, for example, with Brønsted acids and SO_2 by electrophilic addition to the metal–metal bond.[3]

Promising electrophiles emerging from our studies with $C_5H_5Rh(PMe_3)_2$, $C_5H_5Rh(C_2H_4)PMe_3$, $C_5Me_5Rh(CO)_2$, $C_5H_5Co(CO)PMe_3$, etc.[4] are the dihalomethanes, in particular, CH_2I_2 and CH_2Br_2, which react with the mononuclear cyclopentadienylcobalt and -rhodium compounds to form products containing a $M\text{–}CH_2X$ bond. As these products are very useful starting materials for the preparation of complexes with ylides,[4] thio-, seleno-, and telluroformaldehyde,[4d,5] or methylenearsanes (e.g., $CH_2{=}AsPh$)[6] as ligands, we were interested in finding out if the binuclear compounds $[C_5R_5M(\mu\text{-}PMe_2)]_2$ would react similarly with dihalomethanes and whether in this case an oxidative addition of the two fragments, CH_2X and X, to *both* metal atoms would occur. We note in this connection that the rhodium complex $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ reacts with CH_3I to form $[C_5Me_5(CH_3)Rh(\mu\text{-}PMe_2)_2Rh(I)C_5Me_5]$.[7]

The reaction of the cobalt compound $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (**1**) with CH_2I_2, however, takes a different course. After a benzene solution of **1** is stirred with 2 equiv of CH_2I_2, the solvent removed, and the workup procedure described

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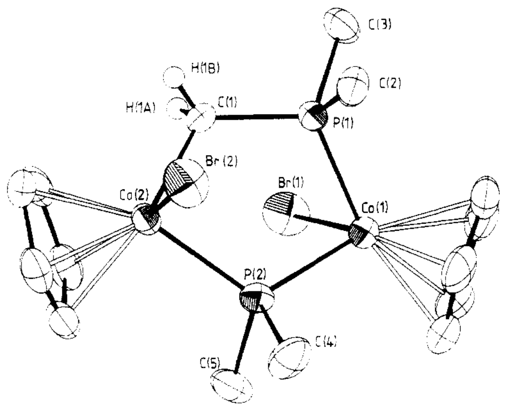


Figure 1. Molecular structure of the trans isomer of the insertion product **5**.

in detail in ref 10 for the synthesis of the bromo derivatives applied, a mixture of compounds is obtained which contains the complexes $[C_5H_5(I)Co(\mu\text{-}PMe_2)]_2$ (**2**) and $[(C_5H_5)_2(I)_2Co_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)]$ (**4**). Whereas **2** can be isolated after chromatography (Al_2O_3, activity V, CH_2Cl_2) in pure form,[8] compound **4** is obtained together with at least one other C_5H_5Co complex which could not be separated by crystallization or chromatographic techniques. Therefore, **4** has been characterized to date by mass spectroscopy and ^1H NMR data.[8,9]

The dibromodicobalt complexes **3** and **5** are formed after addition of a tenfold excess of CH_2Br_2 to a benzene solution of **1** (eq 1).[10] According to the ^1H and ^{31}P NMR spectra,[9] compound **5** is obtained as a 2:1 mixture of cis/trans isomers. As an alternative, the synthesis of **3** as well as that of the iodo analogue **2** can be effected by the reaction of **1** with molecular bromine or iodine (eq 2) which gives the binuclear cobalt(III) complexes in excellent yields.[11] Under mild conditions, no cleavage of the Co–PMe_2–Co bonds by Br_2 or I_2 occurs.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for **5**[a]

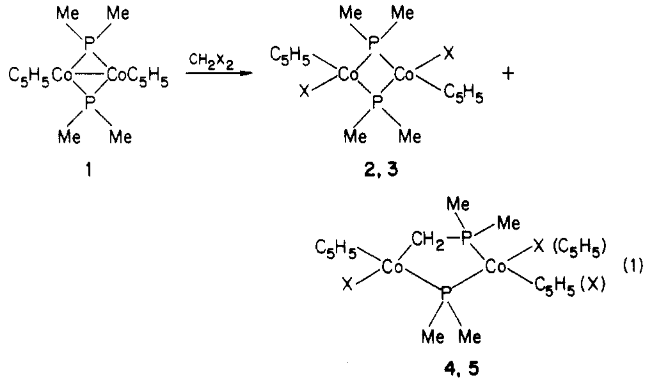
Bond Lengths

Co(1)-Co(2)	3.846 (1)	Co(2)-M(2)	1.712
Co(1)-P(1)	2.167 (2)	P(1)-C(1)	1.797 (7)
Co(1)-P(2)	2.245 (2)	P(1)-C(2)	1.804 (7)
Co(1)-Br(1)	2.388 (1)	P(1)-C(3)	1.836 (7)
Co(1)-M(1)	1.699	P(2)-C(4)	1.843 (7)
Co(2)-C(1)	1.987 (6)	P(2)-C(5)	1.834 (8)
Co(2)-P(2)	2.249 (2)	C(1)-H(1A)	1.03 (5)
Co(2)-Br(2)	2.409 (1)	C(1)-H(1B)	0.88 (7)

Bond Angles

Co(1)-P(1)-C(1)	112.1 (2)	Co(1)-P(1)-C(3)	112.0 (2)
Co(1)-P(2)-Co(2)	117.7 (1)	C(1)-P(1)-C(2)	109.7 (3)
Br(1)-Co(1)-P(1)	89.8 (1)	C(1)-P(1)-C(3)	106.2 (3)
Br(1)-Co(1)-P(2)	91.8 (1)	C(2)-P(1)-C(3)	102.2 (3)
P(1)-Co(1)-P(2)	86.8 (1)	Co(1)-P(2)-C(4)	112.1 (2)
Co(2)-C(1)-P(1)	117.6 (4)	Co(1)-P(2)-C(5)	104.3 (2)
Br(2)-Co(2)-C(1)	93.0 (2)	Co(2)-P(2)-C(4)	107.7 (2)
Br(2)-Co(2)-P(2)	99.8 (1)	Co(2)-P(2)-C(5)	114.3 (2)
C(1)-Co(2)-P(2)	90.1 (2)	C(4)-P(2)-C(5)	99.2 (3)
Co(1)-P(1)-C(2)	114.0 (2)		

[a] Esd in parentheses. M(1) and M(2) are the midpoints of the cyclopentadienyl rings.



2, 4, X = I. 3, 5, X = Br

$$1 + X_2 \rightarrow 2, 3 \qquad (2)$$

The molecular structure of the trans isomer of the insertion product **5** is shown in Figure 1.[12] The most important difference between **5** and the starting material **1** is the large increase in the Co–Co distance from 2.544 (2) Å in **1** to 3.846 (1) Å in **5** which is too long for any metal–metal interaction. Along with the increase of the Co–Co distance, there is a concomitant widening of the Co(1)–P(2)–Co(2) angle from 73.7 (1)° in **1** to 117.7 (1)° in **5**. The Co(1)–P(1)–C(1)–Co(2)–P(2) ring is puckered, the carbon atom C(1) being 0.053 (6) Å below and the phosphorus atom P(1) 0.659 (2) Å above the plane formed by P(2) and

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[8] **2**: MS, *m/e* 624 (M^+). Anal. Calcd for $C_{14}H_{22}Co_2I_2P_2$: C, 26.95; H, 3.55; Co, 18.89. Found: C, 26.98; H, 3.31; Co, 18.92. **3**: MS, *m/e* 532 (M^+, calcd for ^{81}Br). Anal. Calcd for $C_{14}H_{22}Br_2Co_2P_2$: C, 31.73; H, 4.18; Co, 22.24. Found: C, 31.34; H, 4.04; Co, 22.58. **4**: MS, *m/e* 638 (M^+). **5**: MS, *m/e* 546 (M^+, calcd for ^{81}Br). Anal. Calcd for $C_{15}H_{24}Br_2Co_2P_2$: C, 33.12; H, 4.45; Co, 21.67. Found: C, 33.61; H, 4.59; Co, 21.39. **6**: MS, *m/e* 384 (M^+). Anal. Calcd for $C_{15}H_{24}Co_2P_2$: C, 46.90; H, 6.30; Co, 30.68. Found: C, 46.73; H, 6.55; Co, 30.34.

[9] **2**: ^1H NMR ($CDCl_3$, 60 MHz, 298 K) δ 4.72 (s, C_5H_5), 2.19 (vt, N = 14.0 Hz, PMe_2); $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$ (1:1), 90 MHz, 213 K) δ −71.49 (s). **3**: ^1H NMR ($CDCl_3$, 60 MHz, 298 K) δ 4.67 (s, C_5H_5), 1.89 (vt, N = 14.8 Hz, PMe_2); $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$ (1:1), 90 MHz, 213 K) δ −54.83 (s). **4**: ^1H NMR ($CDCl_3$, 60 MHz, 298 K) δ 4.76 (s, C_5H_5), 4.66 (s, C_5H_5), 2.67 (d, J_{HP} = 9.3 Hz, PCH_3), 2.24 (d, J_{HP} = 9.5 Hz, PCH_3), 2.09 (d, J_{HP} = 10.4 Hz, PCH_3), 1.42 (d, J_{HP} = 10.4 Hz, PCH_3), signals for CH_2 protons not observed; $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$ 1:1, 90 MHz, 213 K) δ 74.24 (d, J_{PP} = 29.8 Hz), 48.16 (d, J_{PP} = 29.8 Hz). **5** (first isomer, relative amount 65%): ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ 4.68 (s, C_5H_5), 4.61 (s, C_5H_5), 3.78 (dd, J_{HP} = 9.5, $J_{HH} \simeq$ 9.8 Hz, H_A of CH_2), 2.76 (ddd, J_{HP} = 10.0, J_{HP} = 11.8, $J_{HH} \simeq$ 9.8 Hz, H_X of CH_2), 2.51 (d, J_{HP} = 9.7 Hz, PCH_3), 2.07 (d, J_{HP} = 9.9 Hz, PCH_3), 1.98 (d, J_{HP} = 10.5 Hz, PCH_3), 1.36 (d, J_{HP} = 11.0 Hz, PCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 90 MHz, 223 K) δ 95.93 (d, J_{PP} = 40.2 Hz), 62.52 (d, J_{PP} = 40.2 Hz). **5** (second isomer), relative amount 35%): ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ 4.67 (s, C_5H_5), 4.62 (s, C_5H_5), 3.69 (dd, J_{HP} = 9.0, $J_{HH} \simeq$ 9.5 Hz, H_A of CH_2), 2.69 (ddd, J_{HP} = 10.0, J_{HP} = 11.4, $J_{HH} \simeq$ 9.5 Hz, H_X of CH_2), 2.51 (d, J_{HP} = 9.7 Hz, PCH_3), 1.98 (d, J_{HP} = 10.6 Hz, PCH_3), 1.93 (d, J_{HP} = 10.2 Hz, PCH_3), 1.32 (d, J_{HP} = 11.2 Hz, PCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 90 MHz, 223 K) δ 94.83 (d, J_{PP} = 40.2 Hz), 58.47 (d, J_{PP} = 40.2 Hz). **6**: ^1H NMR (C_6D_6, 400 MHz, 298 K) δ 4.58 (s, C_5H_5), 4.53 (s, C_5H_5), 1.97 (d, J_{HP} = 10.8 Hz, PCH_3), 1.83 (d, J_{HP} = 9.1 Hz, PCH_3), 1.17 (d, J_{HP} = 11.3 Hz, PCH_3), 0.82 (d, J_{HP} = 8.6 Hz, PCH_3), 0.32 (dd, J_{HP} = 10.5, $J_{HH} \simeq$ 9.5 Hz, H_A of CH_2), −1.53 (dd, J_{HP} = 9.0, $J_{HH} \simeq$ 9.5 Hz, H_X of CH_2); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 90 MHz, 213 K) δ 115.62 (s, br), −23.47 (s, br).

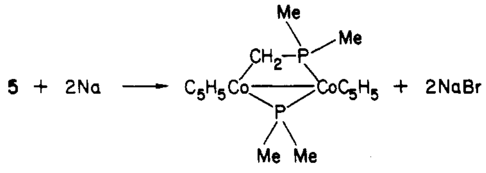
[10] **1** (1.2 g, 3.2 mmol) was dissolved in 10 mL of C_6H_6, and CH_2Br_2 (2.2 mL, 32 mmol) was added. The solution was stirred at 25 °C for 20 h, and the solvent and excess CH_2Br_2 were removed in vacuo. The residue was dissolved in 20 mL of CH_2Cl_2, and the solution was chromatographed under N_2 on Al_2O_3 (Woelm, neutral, activity grade V). With CH_2Cl_2, **3** was separated from **5** and was isolated after repeated chromatography and recrystallization from 1:10 CH_2Cl_2/pentane as dark violet crystals, mp 203 °C dec (yield 450 mg (26%)). Complex **5** was obtained with acetone as solvent and purified in the same way as described for **3**: dark violet crystals; mp 208 °C dec (yield 500 mg (28%)).

[11] **2** and **3** were directly prepared from **1** (370 mg, 1.0 mmol) by dropwise addition of Br_2 or I_2 (1.1 mmol) in benzene (10 mL) at 25 °C. A dark precipitate was formed, which was separated, dissolved in 20 mL of CH_2Cl_2, chromatographed on Al_2O_3 (Woelm, neutral, activity grade V), and recrystallized from 1:10 CH_2Cl_2/pentane; yield 535 mg (86%) for **2** and 420 mg (80%) for **3**. **2** was obtained as dark violet crystals, mp 217 °C dec.

[12] Crystal data for **5**: monoclinic; $P2_1/c$; a = 8.297 (3) Å, b = 17.851 (7) Å, c = 12.907 (4) Å; β = 106.05 (3)°; V = 1832 Å^3; Z = 4; D(calcd) = 1.97 g·cm^{-3}. Intensity data: Syntex P2$_1$ diffractometer, Mo $K\alpha$ (λ = 0.71069 Å) radiation, graphite monochromator; 5° $\le 2\theta \le$ 47°; 2716 reflections; absorption correction, μ = 66.4 cm^{-1}. Solution by direct methods (Multan), refinement of the non-hydrogen atoms by full-matrix least squares, isotropic refinement of H(1A) and H(1B); R_1 = 0.036 and R_2 = 0.043 for 2254 structure factors with $F_o \ge 5.92\sigma(F_o)$. Structure factors for uncharged atoms according to "International Tables of Crystallography", were corrected for anomalous dispersion.

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)

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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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[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%).

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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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