Conclusions

The stabilities of the formyl and hydroxycarbonyl complexes prepared in this study are related to their coordinative saturation and to the steric and electronic conditions at the iridium center. Thus complexes of cis geometry, in which there is a strong steric interaction, tend to be unstable. For example, *cis*-$\mathrm{IrCl(CHO)(dppe)_2^+}$ is not stable above −50 °C and *cis*-$\mathrm{IrCl(CO_2H)(dppe)_2^+}$, the presumed intermediate in the reaction of *cis*-$\mathrm{IrCl(CO_2H)(dppe)_2^{2+}}$ with H_2O and OH^-, is not observable at all. The trans isomers of these formyl and hydroxycarbonyl complexes are more stable and, except for *trans*-$\mathrm{IrCl(CO_2H)(dppe)_2^+}$, can be isolated and characterized. An electronic effect, the increased electron density trans to the hydride ligand, seems to be the major reason for the stability of *trans*-$\mathrm{IrH(CO_2H)(dppe)_2^+}$. This effect also explains the stability of *trans*-$\mathrm{IrH(CHOH)(dppe)_2^{2+}}$ relative to *trans*-$\mathrm{IrCl(CHOH)(dppe)_2^{2+}}$. The complex *trans*-$\mathrm{IrH(CHOH)(dppe)_2^{2+}}$ is in turn more stable in solution than the formyl complex $\mathrm{IrH(CHO)(dppe)^{2+}}$. This increased stabilization in the presence of a Lewis acid is probably a result of suppression of the usual modes of decomposition that formyl complexes exhibit, i.e., hydride migration to the metal and hydride transfer reactions, and suggests that hydroxycarbene complexes could be very important intermediates in the reduction of carbon monoxide.

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Registry No. I, 91606-11-0; II, 94570-04-4; IIIa, 91685-25-5; IIIb, 94596-64-2; IV, 66673-10-7; V, 91685-23-3; VI, 66350-34-3; VII, 94570-06-6; VIIIa, 94570-08-8; VIIIb, 94570-15-7; IXa, 94570-10-2; IXb, 94570-17-9; X, 94570-12-4; *trans*-$\mathrm{[IrCl(CO)(dppe)_2]Cl_2}$, 94570-13-5; $\mathrm{Ir(CO)(dppe)_2^+}$, 40264-88-8; *cis*-$\mathrm{IrH_2(dppe)_2^+}$, 47898-62-4; LiB(*sec*-Bu)$_3$H, 38721-52-7; $\mathrm{LiBEt_3D}$, 74540-86-6; $\mathrm{Ir(dppe)_2^+}$, 29871-99-6; $\mathrm{IrH(dppe)_2^{2+}}$, 66350-22-9; CO, 630-08-0; $\mathrm{[IrH(CHOH)(OEt_2)(dppe)_2][BF_4]_2}$, 94570-19-1; $\mathrm{LiBEt_3H}$, 22560-16-3.

Communications

New Bimetallic Cobalt(II) Complexes of Chelated, Bridged Phosphido Ligands

Loren Chen, Dennis J. Kountz, and Devon W. Meek*

Department of Chemistry
and the Materials Research Laboratory
The Ohio State University, Columbus, Ohio 43210

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Summary: Treatment of cobaltocene with secondary phosphines (e.g., R_2PH or the linked bis(secondary diphosphines) $\mathrm{H(Ph)P(CH_2)_{\mathit{n}}P(Ph)H}$, $n = 2, 3$) produces phosphido-bridged dicobalt complexes **1**–**5** that contain a Co–Co bond. Reactions of **1**–**5** with SO_2 at ambient conditions lead to insertion of SO_2 into the Co–Co bond, whereas $HBF_4{\cdot}OEt_2$ produces dicobalt cations in which the bridging hydrogen atom bonding can be represented as a closed two-electron, three-center interaction.

Our research group has recently shown that tertiary–secondary diphosphine ligands of the type $\mathrm{R_2PCH_2CH_2CH_2P(H)Ph}$ provide rational and controlled routes to phosphido-bridged bimetallic complexes.[1] Syntheses of phosphido and arsenido-bridged compounds have become an active field of research based on the reasonable assumption that these compounds would possess strong binding properties and help maintain the integrity of $\mathrm{M{-}PR_2{-}M}$ bridges in bimetallic complexes and small metal clusters.[2] However our results,[2d] as well as several other recent reports,[2a,3-5] indicate that $\mathrm{M{-}PR_2{-}M}$ bridges are more reactive than previously thought. We have attempted to improve the stability of the bridging phosphido linkage by incorporating it into the chain of a chelating ligand.[1] Flood[6a] reported the first example of a linked (i.e., via a trimethylene chain) phosphido bridge; two other reports have appeared recently, in which bridging phosphido ligands are connected by *o*-phenylene[6b] and *o*-xylene[6c] linkages in iron carbonyl complexes. Herein, we report the syntheses, ^{31}P NMR data, and the structures of dicobalt complexes of linked bridging bis(phosphido) ligands.

Hayter,[7] Werner,[8] Dahl,[9] and their co-workers have prepared and studied the binuclear complexes $[(C_5R_5)M$-

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[1] (a) Meek, D. W.; Waid, R. D.; Tau, K. D.; Kirchner, R. M.; Morimoto, C. N. *Inorg. Chim. Acta* **1982**, *64*, L221–L223. (b) Glaser, R.; Kountz, D. J.; Gallucci, J. C.; Meek, D. W. *Inorg. Chim. Acta* **1983**, *77*, L207–L209. (c) Glaser, R.; Kountz, D. J.; Waid, R. D.; Gallucci, J. C.; Meek, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 6324–6333.

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[4] (a) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53–59. (b) Harley, A. D.; Whittle, R. R.; Geoffroy, G. L. *Ibid.* **1983**, *2*, 383–387. (c) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519.

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[8] (a) Werner, H.; Hoffmann, W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 158. (b) Hoffmann, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1014. (c) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

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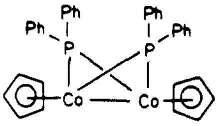
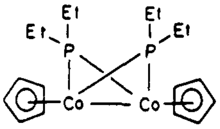
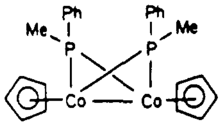
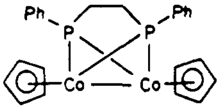
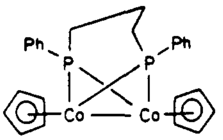
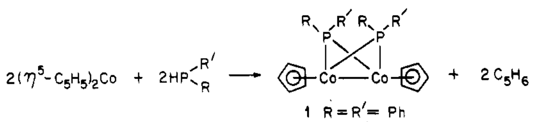
Table I. Proton and $^{31}P\{^1H\}$ NMR Spectral Data on the Cobalt(II) Phosphido-Bridged Complexes[a]

parent dicobalt complex			SO₂ reaction product			protonated complex				
		$\delta(^{31}P)$		$\delta(^{31}P)$	Δ(insertn)		$\delta(^{31}P)$	$\delta(^1H)$	$^3J_{PH}$, Hz	Δ(protonatn)
	1	119.6	6	−75.7	−195.3	11	132.0	−19.2 (t)[b]	55.5	12.4
	2	133.4	7	−61.4	−194.8	12	169.7	−21.2 (t)	56.0	36.3
	3	112.8	8	−82.0	−194.8	13	138.0	−20.0 (t)	58.4	25.2
	4	139.7	9	−12.7	−152.4	14	161.7	−21.0 (t)	51.5	22.0
	5	97.7	10			15	120.8	−19.8 (t)	51.0	23.1

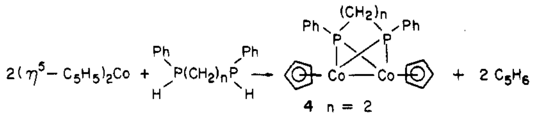
[a] The proton and phosphorus-31 chemical shifts are referenced to internal Me_4Si and external 85% H_3PO_4, respectively. [b] t = triplet.

(μ-PR'_2)]$_2$ (M = Co, R = H, and R′ = CH_3, C_6H_5; M = Rh, R = R′ = CH_3). These complexes have a bent M_2P_2 core geometry,[9] and the metal–metal bonds are susceptible to cleavage by electrophilic attack by Lewis acids.[8]

In order to determine the effect of linked (e.g., a $(CH_2)_n$ chain between the phosphorus atoms) diphosphido bridges as compared to two unlinked R_2P^- bridges, we have prepared and characterized a series of dicobalt complexes containing two R_2P^- bridges or one $(RP(CH_2)_nPR)^2$ bridge. For example, by refluxing the secondary phosphines, R′(R)PH (R = R′ = Ph; R = R′ = Et; R = Me, R′ = Ph) or the bis(secondary phosphines) H(Ph)P$(CH_2)_n$P(Ph)H (*n* = 2, 3) with cobaltocene, compounds 1–5 are obtained (eq 1 and 2).



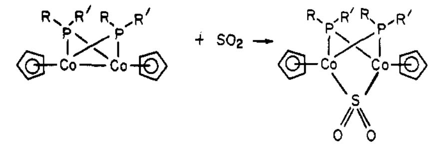
1 R = R′ = Ph
2 R = R′ = Et
3 R = Me, R′ = Ph



4 n = 2
5 n = 3

The ^{31}P NMR chemical shifts of compounds 1–5 (Table I) appear significantly downfield from the 85% H_3PO_4 standard; a large downfield shift is characteristic of a metal–metal bond.[2d,10] Interestingly, the ^{31}P NMR resonance of 4 occurs further down field from that of 5 which should have similar chemical and inductive properties to 4. The downfield shift is attributed to the "five-membered ring effect".[11]

When the dichloromethane solutions of 1, 2, 3, 4, and 5 were treated with SO_2, adducts 6, 7, 8, 9, and 10 were formed, respectively (eq 3).[12] Complexes 6, 7, 8, and 9 are



deep green when dissolved in dichloromethane; complex 10 is so insoluble in common organic solvents that spectroscopic studies have been prevented to date. The ^{31}P NMR resonances of 6, 7, 8, and 9 (Table I) occur upfield from the H_3PO_4 standard. These large changes in the $\delta(^{31}P)$ values suggest that the SO_2 group has inserted into the Co–Co bond; this point has been confirmed by the X-ray structural determination of the [(C_5H_5)Co(μ-PEt_2)]$_2$(μ-SO_2) complex.[13] The insertion chemical shifts (the difference between the ^{31}P NMR chemical shifts of the SO_2 adduct and its corresponding parent complex) are

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(10) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349–1354.

(11) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

(12) All of the new compounds reported herein have satisfactory microanalyses (done by MHW Laboratories, Phoenix, AZ).

(13) The crystal structure of one of the SO_2 products 7 has been determined by X-ray diffraction. Compound 7, $(C_5H_5)_2Co_2(\mu\text{-}PEt_2)_2(\mu\text{-}SO_2)$, crystallizes in space group $P2_1/c$, $Z = 4$, with dimensions $a = 9.618$ (2) Å, $b = 13.619$ (3) Å, $c = 16.831$ (4) Å, and $\beta = 110.32$ (2)° at 145 K. The SO_2 group is inserted into the Co–Co bond; the Co1–Co2 distance in 7 is 3.0686 (3) Å. The Co–S distances (2.1724 (6) and 2.1768 (6) Å) and the Co–P distances (2.2080 (6), 2.2242 (6), 2.2200 (6), and 2.2136 (6) Å) are consistent with the expected values. The details of the structures of both 7 and 15 will be submitted to *Inorg. Chem.*

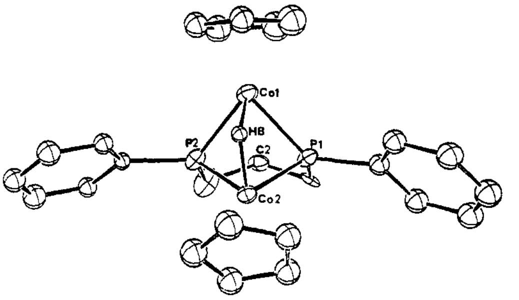

Figure 1. ORTEP drawing of a perspective view of the cation **15a** without the organic hydrogen atoms.

listed in Table I. These values seem to be relatively independent of the substituents on the phosphido group. However, the insertion chemical shift of the "chelate-phosphido bridged" compound 4 is significantly smaller than the values of all the other complexes that do not contain a linked phosphido bridge.

When the complexes 1–5 are treated with $HBF_4 \cdot OEt_2$, the corresponding cationic complexes $[(C_5H_5)Co(\mu\text{-}PR_2)_2(\mu\text{-}H)Co(C_5H_5)]BF_4$ (11–15), are formed. The ^{31}P NMR resonances of these complexes are shifted even further downfield than their parent complexes (Table I); thus, it is concluded that a strong cobalt–cobalt interaction still exists in these bridging hydride cationic complexes. The ^1H NMR chemical shifts of the bridging hydride atom and the $^2J_{P-H}$ coupling constants fall within a narrow range. The mode of bonding between the two cobalt atoms and the bridging hydride may be described as a closed two-electron, three-center interaction.[14] However, the protonation chemical shifts (the difference in ^{31}P NMR chemical shifts between the parent and the protonated complex (Table I)) seem to be related to the inductive effect of the substituents on the phosphido group. The magnitude of the protonation chemical shift increases as the number of aromatic substituents on the bridging phosphorus atom decreases.

X-ray-quality, olive-green crystals of $[(C_5H_5)Co(\mu_2\text{-}PPhCH_2CH_2CH_2PPh)(\mu\text{-}H)Co(C_5H_5)]^+BF_4^-$ were grown by allowing hexane to diffuse slowly into a CH_2Cl_2 solution of 15.[15] The structural determination shows that two crystallographically independent cations **15a** and **15b** and two crystallographically independent BF_4 anions exist in the solid-state structure. Except for one disordered cyclopentadienyl ring in **15b**, and the dihedral angle between the phenyl rings (113 (1)° in **15a** and 177 (1)° in **15b**), the internal structures of **15a** and **15b** are nearly identical. An ORTEP drawing of **15a** is given in Figure 1. The average Co–Co distance (2.516 (3) Å) is comparable to that (2.517 (1) Å) found in $[(C_5H_5)Co(\mu\text{-}P(CH_3)_2)_2(\mu\text{-}H)Co(C_5H_5)]^+[B(C_6H_5)_4]^-$, **16**,[9b] but shorter than the unprotonated molecules $(C_5H_5)Co(\mu\text{-}P(C_6H_5)_2)_2Co(C_5H_5)$, **17**,[9b] 2.551 (4) Å, and $(C_5H_5)Co(\mu\text{-}P(CH_3)_2)_2Co(C_5H_5)$, **18**,[8b] 2.544 (2) Å. The trimethylene bridge between the phosphorus atoms in **15a**/**15b** apparently holds the phosphorus atoms closer together, 2.742 (6) Å, than found in complexes **16**, 2.937 (3) Å, **17**, 2.856 (3) Å, and **18**, 2.861 (8) Å, where the phosphido groups are not linked together. The six-membered heterocyclic ring $\overline{P2\text{-}Co\text{-}P1\text{-}C1\text{-}C2\text{-}C3}$ adopts classical cyclohexane boat and chair conformations simultaneously in **15a**/**15b**, thereby reducing the dicobalt complex to C_s symmetry. For the boat conformation the average Co1–C2 distance is 3.48 (2) Å, whereas the Co2–C2 distance for the chair conformation is 3.91 (2) Å. The average Co–P distance, 2.150 (4) Å, is consistent with Co–P distances found in the structures of **16**, **17**, and **18**.[9b]

The cyclopentadienyl rings in **15a**/**15b** are nearly eclipsed. The Co–C distances range from 2.00 (3) to 2.13 (2) Å, similar to the Co–C distances found in **16**, **17**, and **18**.[9b] Protonation of the Co–Co bond forces the cyclopentadienyl ring centroids to align closer to the Co–Co internuclear vector. The angle between the cyclopentadienyl ring centroids is 149 (4)° in **15a**/**15b** vs. 120° in **18**;[9b] the corresponding angle in **16** is 154°. The average Co–H dis-

Table II. Bonded and Selected Nonbonded Distances (Å) 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
Co1–Co2	2.512 (2)	2.520 (2)
Co1–P1	2.157 (4)	2.156 (4)
Co1–P2	2.152 (4)	2.153 (4)
Co1–H	1.73 (11)	1.54 (12)
Co2–P1	2.135 (4)	2.147 (4)
Co2–P2	2.146 (4)	2.149 (4)
Co2–H	1.54 (12)	1.73 (11)
Co1· · ·C2	3.470 (12)	3.485 (13)
Co2· · ·C2	3.909 (13)	3.919 (11)
P1· · ·P2	2.737 (4)	2.747 (4)
Co1–CP11	2.041 (7)	2.052 (8)
Co1–CP12	2.048 (8)	2.050 (8)
Co1–CP13	2.082 (9)	2.091 (8)
Co1–CP14	2.097 (9)	2.119 (9)
Co1–CP15	2.073 (9)	2.095 (8)
Co2–CP21	2.041 (9)	2.030 (21), 2.052 (36)[a]
Co2–CP22	2.043 (9)	2.025 (19), 2.001 (30)
Co2–CP23	2.077 (9)	2.088 (25), 2.040 (31)
Co2–CP24	2.096 (8)	2.130 (23), 2.112 (29)
Co2–CP25	2.074 (9)	2.095 (17), 2.119 (44)

[a] Two values for the disordered cyclopentadienyl ring with contribution A and B, respectively.

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(14) (a) Bau, R.; Teller, R. G.; Kirtley, D. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, 176. (b) Bau, R.; Koetzle, T. F. *Pure Appl. Chem.* **1978**, *50*, 55. (c) Teller, R. G.; Bau, R. *Struct. Bonding* (*Berlin*) **1981**, *44*, 1 and references contained therein.

(15) Unit cell dimensions $a = 9.581$ (2) Å, $b = 15.489$ (4) Å, $c = 32.926$ (10) Å, and $\beta = 92.93$ (2)° were found at 150 K for the space group $P2_1/n$ (alternative setting of C_{2h}^5—$P2_1/c$, No. 14), $Z = 8$. Bragg intensity data were collected on a Syntex P$\bar{1}$ diffractometer (graphite-monochromated Mo Kα radiation, $4.0° \leqslant 2\theta \leqslant 42.0°$) by the ω scan method. The data were treated in the usual manner,[16] and an analytical absorption correction was applied.[17] MULTAN80[18] was used to locate the cobalt atoms in each crystallographically independent cation. The remaining non-hydrogen atoms were found by standard Fourier techniques. Phenyl rings ($d_{C-C} = 1.395$ Å) and cyclopentadienyl rings ($d_{C-C} = 1.420$ Å) were refined as rigid bodies. Cobalt, phosphorus, and carbon atoms belonging to the $-CH_2CH_2CH_2-$ chain of the phosphorus ligand were refined anisotropically while all other non-hydrogen atoms were refined with isotropic thermal parameters. The bridging hydride atoms in **15a**/**15b** were refined satisfactorily with isotropic thermal parameters; all other hydrogen atoms were placed at calculated positions ($d_{C-H} = 0.95$ Å, $B(H) = B_{iso}(C) + 1.0$ Å^2). Full-matrix least-squares refinement converged at $R(F_o) = 0.057$ and $R_w(F_o) = 0.053$ [295 parameters and 2910 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$].[19]

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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.

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

Helmut Werner* and Ralf Zolk

Institut für Anorganische Chemie der Universität
Am Hubland, D-8700 Würzburg, Germany

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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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[1] Part 50 of the series: "Basic Metals". Part 49: Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.*, accepted for publication.

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