# Reactions of a Bulky Dichlorophosphine with Tetracarbonylcobaltate and Bis($\eta^5$-cyclopentadienyl)bis($\mu$-carbonyl)dicobaltate Anions. A $Co_4$ Cluster with Two Different Phosphinidenes and an Unusual $Co_2P$ Ring System

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*Summary:* The reaction of $(Me_3Si)_2CHPCl_2$ (**1**) with $Na[Co(CO)_4]$ affords $Co_4(\mu_4\text{-}PCH(SiMe_3)_2)(\mu_4\text{-}PCH_2SiMe_3)(\mu\text{-}CO)_2(CO)_8$ (**2**), a cluster with two different phosphinidenes, and $Co_3(\mu_3\text{-}PCH(SiMe_3)_2)(CO)_9$ (**3**). The reaction of **1** with $Na[Co_2(\eta^5\text{-}C_5H_5)_2(CO)_2]$ produces $Co_2\{\mu\text{-}P(H)CH(SiMe_3)_2\}(\eta^5\text{-}C_5H_5)(CO)_4$ (**4**). The structures of **2**, **3**, and **4** have been determined by X-ray crystallography.

The reaction of dihalophosphines with $Na[Co(CO)_4]$ or $Co_2(CO)_8$ results in $\{Co(CO)_4\}_4PPh$[1] or clusters $Co_3(\mu_3\text{-}PR)(CO)_9$ (R = Ph, *t*-Bu, $Et_2N$)[2,3] and $Co_4(\mu_4\text{-}PPh)_2(\mu\text{-}CO)_2(CO)_8$.[4] Anticipating that new types of product might result from the use of bulkier phosphine substituents, we treated $(Me_3Si)_2CHPCl_2$[5] with $K[Co(CO)_4]$[6] and $Na[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[7] Both reactions were conducted by dropwise addition of a THF solution of $(Me_3Si)_2CHPCl_2$ to a THF solution of the organometallic anion at −40 °C. Separation of the crude reaction mixtures was effected by column chromatography (silica gel/*n*-hexane). The products of the $K[Co(CO)_4]$ reaction were identified as $Co_4(\mu_4\text{-}PCH(SiMe_3)_2)(\mu_4\text{-}PCH_2SiMe_3)(\mu\text{-}CO)_2(CO)_8$ (**2**, red) and $Co_3(\mu_3\text{-}PCH(SiMe_3)_2)(CO)_9$ (**3**, green) by X-ray crystallography.[8] The metric parameters for the skeletons of **2** and **3** are similar to those for the analogous PPh compounds.[3,4] The significance of **2** (Figure 1) is that it features two different phosphinidenes in the same cluster.[10] Presumably, the $Me_3SiCH_2$ group arises via nucleophilic attack of a $Me_3Si$ group of $(Me_3Si)_2CH$, followed by protonation of the resulting carbanion. Previously reported transformations of this type include $(Me_3Si)_3C \rightarrow (Me_3Si)_2CH$[11] and $(Me_3Si)_2CH \rightarrow CH_3$.[12] Although two $^{31}P$ NMR chemical shifts should be discernible for **2**, only one very broad ($^{59}$Co-coupled) resonance was detected at 156 ppm. Compound **3** is paramagnetic.

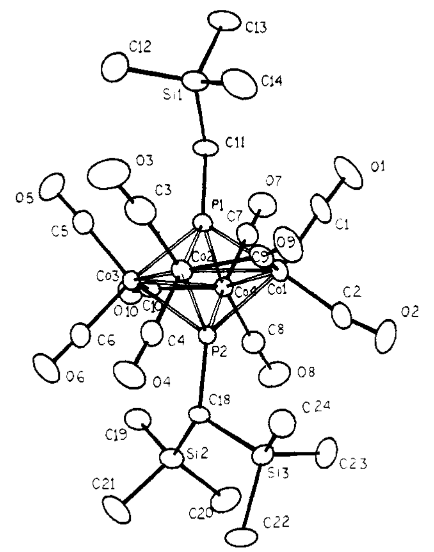

**Figure 1.** ORTEP drawing of $Co_4(\mu_4\text{-}PCH(SiMe_3)_2)(\mu_4\text{-}PCH_2SiMe_3)(\mu\text{-}CO)_2(CO)_8$ (**2**). Important parameters: P(1)–C(11) = 1.835 (4), P(2)–C(18) = 1.848 (4), P(1)–Co(1) = 2.333 (1), P(1)–Co(2) = 2.270 (1), P(1)–Co(3) = 2.210 (1), P(1)–Co(4) = 2.264 (1), P(2)–Co(1) = 2.306 (1), P(2)–Co(2) = 2.286 (1), P(2)–Co(3) = 2.309 (1), and P(2)–Co(4) = 2.231 (1) Å.

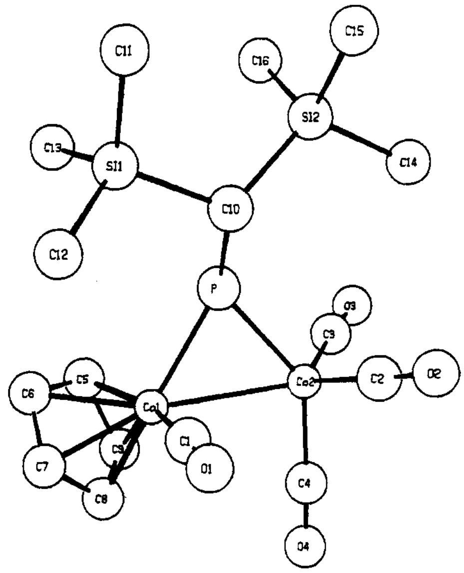

**Figure 2.** ORTEP drawing of $Co_2\{\mu\text{-}P(H)CH(SiMe_3)_2\}(\eta^5\text{-}C_5H_5)(CO)_4$ (**4**). Important parameters: Co(1)–P = 2.163 (8), Co(2)–P = 2.148 (7), and Co(1)–Co(2) = 2.582 (7) Å; Co(1)–P–Co (2) = 125.3 (8), Co(1)–Co(2)–P = 53.5 (3), and Co(2)–Co(1)–P = 52.9°.

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[8] Complex **2**: $C_{21}H_{30}Co_4O_{10}P_2Si_3$, $M_r$ = 824.41; triclinic; $P\bar{1}$; $a$ = 9.096 (1) Å, $b$ = 12.100 (3) Å, $c$ = 15.968 (2) Å; $\alpha$ = 101.51 (2)°, $\beta$ = 92.91 (1)°, $\gamma$ = 95.56 (2)°; $V$ = 1710 (1) Å$^3$; $Z$ = 2; $D$(calcd) = 1.601 g cm$^{-3}$.
Complex **3**: $C_{16}H_{19}Co_3O_9PSi_2$, $M_r$ = 619.27; monoclinic, $P2_1/n$; $a$ = 9.397 (1) Å, $b$ = 17.429 (2) Å, $c$ = 16.031 (2) Å; $\beta$ = 97.13 (1)°; $V$ = 2606 (1) Å$^3$; $Z$ = 4; $D$(calcd) = 1.578 g cm$^{-3}$.
Complex **4**: $C_{16}H_{25}Co_2O_4PSi_2$: orthorhombic, $Pca2_1$ (No. 29); $a$ = 16.686 (4) Å, $b$ = 28.859 (2) Å, $c$ = 9.412 (3) Å; $V$ = 4531 (1) Å$^3$; $Z$ = 8; $D$(calcd) = 1.424 g cm$^{-3}$. Intensity data: Enraf-Nonius CAD 4-F diffractometer, $\omega$-$2\theta$ scan mode in the range $3.0 \leq 2\theta \leq 46.0$; 3370, 3760, and 4494 unique reflections for **2**, **3**, and **4**, respectively. Empirical absorption corrections were applied in each case. The structures of **2**, **3**, and **4** were solved by direct methods (MULTAN)[9] and refined (full-matrix least squares) by use of 3207, 1623, and 1553 data, respectively. Final residuals were as follows: **2**, $R$ = 0.0399, $R_w$ = 0.0504; **3**, $R$ = 0.0564, $R_w$ = 0.0686; **4**, $R$ = 0.072, $R_w$ = 0.079.

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[10] Professor Othmar Stelzer had kindly informed us of the synthesis of an iron complex involving two different phosphinidenes.

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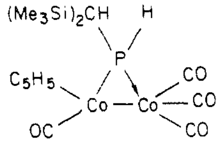
The red crystalline product of the $Na[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ reaction was identified as the $Co_2P$ ring compound 4 by X-ray diffraction methods (Figure 2).[8] Although the hydrogen on phosphorus was not evident in the X-ray study, its presence was established by the detection of a parent peak in the EI mass spectrum and by the diamagnetism of the compound.[13] Moreover, even though $^{31}P$–$^{1}H$ coupling could not be detected in the $^{31}P$ NMR spectrum due to the breadth of the signal, the chemical shift of +144 ppm is consistent with the phosphido bridge formulation. We do not have any evidence regarding the mechanism of formation of 4. However, it is possible that this compound arises from an initially formed terminal phosphinidene complex via either of the mechanisms shown.[14] The source of the $Co(CO)_3$ unit is presumable the $[Co(CO)_4]^-$ anion which is always present in solutions of $Na[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[7]



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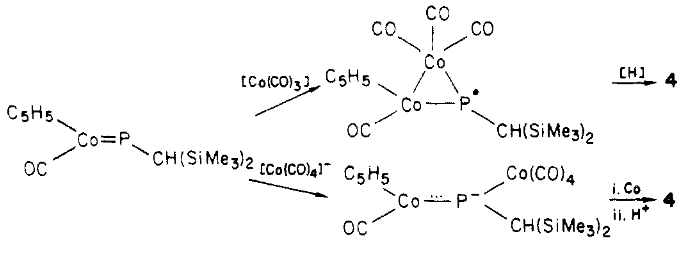

**Acknowledgment.** We are grateful to the National Science Foundation, the Robert A. Welch Foundation, and the Science and Engineering Research Council for financial support.

**Supplementary Material Available:** Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 2, 3, and 4 (59 pages). Ordering information is given on any current masthead page.

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(13) As is clear from the ratio of the number of observed to the number of total reflections, the crystals of 4 did not diffract strongly. We can, however, detect the hydrogen on phosphorus in the recently prepared analogue $Co_2[\mu\text{-}P(H)CH(SiMe_3)_2](\eta^5\text{-}C_5Me_5)(CO)_4$, and the P–H bond length is 1.36 (9) Å. Arif, A. M.; Cowley, A. H.; Pakulski, M., to be submitted for publication.

(14) We are indebted to a reviewer for suggesting the ionic mechanism.

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# Bis(triphenylphosphine)platinum Complexes of Cycloheptatetraene, Benzocycloheptatetraene, and Dibenzocycloheptatetraene

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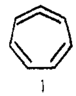
*Summary:* Addition of a mixture of isomeric bromocycloheptatrienes, 1,2-benzo-4-bromocycloheptatriene, or 1,2,3,4-dibenzo-6-bromocycloheptatriene to a THF solution of tris(triphenylphosphine)platinum and potassium *tert*-butoxide gives the corresponding cycloheptatetraene complexes **7**, **8**, and **9**. These are the first such complexes to exist in the allene form; all previous examples preferred tropylium ion structures.

It is now well established that allene 1 is energetically preferred over its planar isomer 2 while in complexes of this ligand with Fe(II), Ru(II), or W(0), the opposite preference is shown; 3 is favored over 4.[1-9] This change in structural preference is convincingly rationalized for the $Fp^+$ (Fp = ($\eta^5$-cyclopentadienyl)dicarbonyliron) complex by EHMO calculations which forecast the carbene (or tropylium) structure to lie significantly below its allene isomer.[10] Calculations at the same level make the interesting prediction that the structural preference should be reduced to no difference for the corresponding $(H_3P)_2Pt$ complex. We took these results to suggest that a Pt(0) complex of $C_7H_6$ might prefer structure 5 over 6. At this time we report the synthesis of 7–9, all of which exist exclusively as allene complexes.



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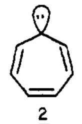

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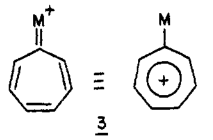

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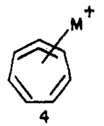

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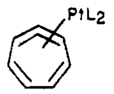
M=CpFe(CO)$_2$ ; CpRu(CO)$_2$ ; (CO)$_5$W$^-$



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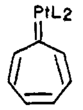

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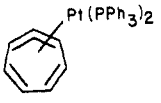

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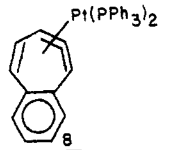

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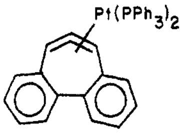

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(10) Details of this work will be published elsewhere.

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