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Preliminary communication

PHOSPHAACETYLENEHEXACARBONYLDICOBALT COMPLEXES: NEW CLUSTER LEWIS BASES

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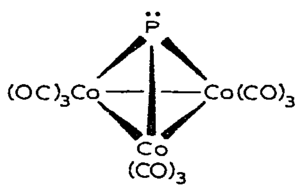
Summary

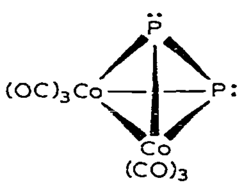
The reaction of $RCCl_2PCl_2$ ($R = CH_3$, C_6H_5, $(CH_3)_3Si$) with dicobalt octacarbonyl in THF at —78°C gave the new $(RCP)Co_2(CO)_6$ complexes, which contain the $CPCo_2$ cluster unit, as air-sensitive red oils. The complex with $R = CH_3$ reacted with $(OC)_5M{\cdot}THF$ to give the corresponding $M(CO)_5$ ($M = Cr$, W) adducts and the complex with $R = C_6H_5$ could be acetylated in the *para* position with $CH_3C(O)Cl/AlCl_3$.

Phosphidocobalt carbonyl cluster complexes of type $P_n[Co(CO)_3]_{3-n}$ ($n = 1$, 2 and 3), which contain an approximately tetrahedral core of phosphorus and cobalt atoms, have been prepared and studied by Hungarian workers [1,2,3]. The diphosphido complex II was stable [1], but the monophosphido complex I could not be isolated since it underwent "cyclotrimerization" by intermolecular carbon monoxide displacement to give $[PCo_3(CO)_8]_3$ [2]. That the phosphorus atom of I is an effective donor site was demonstrated also by the preparation of $(OC)_9Co_3PFe(CO)_4$ by its reaction with $Fe_2(CO)_9$ in THF [2].

As a result of our studies of the chemistry of alkylidynetricobalt nonacarbonyl complexes, $RCCo_3(CO)_9$ (III) [4], we became interested in the possibility of combining the phosphorus function of I with the organic function of III in one cluster molecule, IV. Such hybrid organophosphorus—cobalt carbonyl clusters may be viewed as the hexacarbonyldicobalt complexes of the respective phosphaacetylenes, $RC{\equiv}P$, a class of rather unstable organophosphorus compounds which to date numbers only a few members [5]. Accordingly, we write them as $(RCP)Co_2(CO)_6$, in analogy to the acetylenehexacarbonyldicobalt complexes, $(RC_2R)Co_2(CO)_6$ (V). A series of complexes of type IV with differing R substituents on carbon, in which the phosphorus atom is a site of Lewis basicity, would be interesting and possibly useful ligands in transition metal chemistry. Variation in R could bring vari-



(I)



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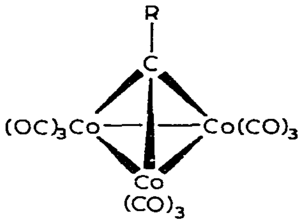

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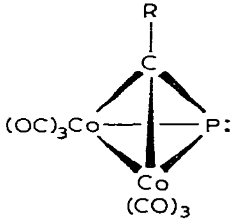
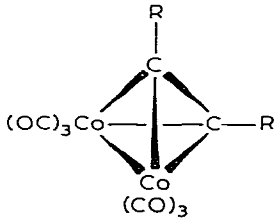
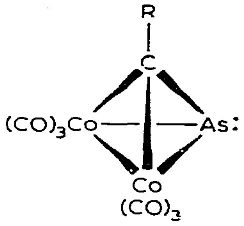


(IV)



(V)



(VI)

ations in Lewis basicity as electronic and steric factors associated with R are changed.

We have prepared three cluster compounds of type IV with R = CH_3 (IVa), R = C_6H_5 (IVb) and R = $(CH_3)_3Si$ (IVc) using the procedure which we successfully applied to the preparation of the arsenic analogs, VI [6] (eq. 1—3). The substituted α,α-dichloroalkyldichlorophosphines were not isolated, but rather the THF solutions in which they had been prepared were added to

$$RCCl_2Z + n\text{-}C_4H_9Li \xrightarrow{-100^\circ C} RCCl_2Li + n\text{-}C_4H_{10} \tag{1}$$

(R = CH_3 or $(CH_3)_3Si$; Z = H. R = C_6H_5 ; Z = Cl)

$$RCCl_2Li + PCl_3 \xrightarrow{-100^\circ C} RCCl_2PCl_2 + LiCl \tag{2}$$

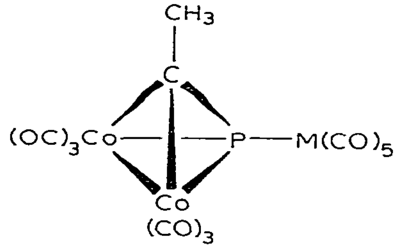
$$RCCl_2PCl_2 + Co_2(CO)_8 \xrightarrow{-78^\circ C} (RCP)Co_2(CO)_6 \tag{3}$$

dilute solutions of dicobalt octacarbonyl in THF at —78°C. At about —10"C moderate CO evolution occurred and subsided after about 30 min. After 18 h at room temperature, the solvents were removed at reduced pressure and the residue was extracted with pentane. In the case of $(CH_3CP)Co_2(CO)_6$ (IVa) the brown oil thus obtained after evaporation of the pentane was chromatographed (silicic acid/pentane) and subsequently distilled at 45°C at 0.2 Torr (short path still). The product, a red oil, was obtained in 27% yield, based on starting 1,1-dichloroethane. (Found: C, 27.74; H, 0.99%. $C_8H_3O_6PCo_2$ calcd.: C, 27.94; H, 0.88%). It was found to be fairly air-sensitive but moderately stable in solution under nitrogen. Its spectroscopic properties are similar to those of $(CH_3CAs)Co_2(CO)_6$ [6]. IR (CCl_4): three strong bands in the terminal carbonyl region at 2100, 2060 and 2036 cm^{-1}. ^1H NMR (CCl_4): doublet (J 4 Hz) at δ 2.90 ppm. ^{13}C NMR ($CDCl_3$): δ_C 26.4 (s, CH_3), 144.4 (d, J 258 Hz, apical carbon atom) and 199.9 ppm (s, CO). ^{31}P NMR ($CDCl_3$), broad singlet with four peaks centered at δ_P 64.0 ppm (downfield from external 85% H_3PO_4). An orange, crystalline mono-triphenylphosphine substitution product, m.p. 108—110°C, could be prepared. Its 70 eV mass spectrum showed the molecular ion and fragments corresponding to successive loss of the six CO ligands.

Complexes IVb and IVc were isolated in similar fashion in lower yield (18 and 8%, respectively) as air-sensitive red oils. Both were characterized spectroscopically and converted to their bis-triphenylphosphine substitution products. The latter gave correct C and H analyses.

In contrast to its arsenic analog, $(CH_3CP)Co_2(CO)_6$ reacts readily with the pentacarbonyl-chromium(0)- and -tungsten(0)-tetrahydrofuran adducts to give complexes of type VII. Both complexes are purple-red, air-stable, crystalline solids. The IR spectrum of the pentacarbonyltungsten adduct showed $\nu(C\equiv O)$ at 2112m, 2080vs, 2055s, 1996w, 1992w and 1960vs cm^{-1} (in $CHCl_3$) and its mass spectrum contained fragment ions corresponding to the successive loss of all eleven CO ligands.

Like its arsenic analog, $(C_6H_5CP)Co_2(CO)_6$ can be acetylated in the *para* position by the $CH_3C(O)Cl/AlCl_3$ reagent. The product, $[p\text{-}CH_3C(O)\text{-}C_6H_4CP]Co_2(CO)_6$, a red oil, was isolated in 43% yield. Its IR spectrum (CCl_4) showed three strong bands in the terminal carbonyl region at 2100, 2065 and 2040 cm^{-1} and its ketone carbonyl stretching frequency at 1680 cm^{-1}. It was converted to the crystalline 1,2-bis-triphenylphosphine substitution product, m.p. 115—116.5°C. Like their arsenic analogs, complexes IVa and IVb do not react with iodomethane.



(VIIa) M = Cr, m.p. 65–66.5 °C

(VIIb) M = W, m.p. 77–79 °C

It is apparent that a marked gain in stability results when one $Co(CO)_3$ unit in I is replaced by an RC group. Such RC-for-$Co(CO)_3$ substitution does not suppress the donor properties of the phosphorus atom in IV, and it is likely that an interesting coordination chemistry of these new C/P/Co cluster complexes can be developed. A comparison of the $(RCP)Co_2(CO)_6$ complexes with their $(RCAs)Co_2(CO)_6$ analogs is of interest, and some differences are readily apparent. The latter are air-stable; the former are not. The phosphorus-containing clusters show donor activity; those containing arsenic do not react with $(OC)_5Cr\cdot THF$ or the analogous molybdenum complex. Further comparative investigations of the chemistry of complex series IV and VI is in progress.

Acknowledgement

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