

Heteronuclear Cluster Systems. Part 12.† Synthesis of μ -Phenylphosphinediyl-bis(tetracarbonylcobalt) and 1,1,1,2,2,2,3,3,3-Nonacarbonyl- μ_3 -phenylphosphinediyl-*triangulo*-dicobaltiron

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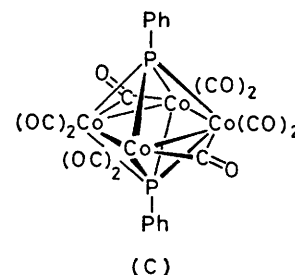
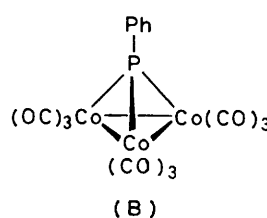
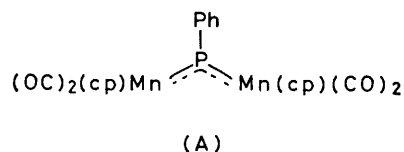
The reaction of $\text{Na}[\text{Co}(\text{CO})_4]$ with PPhCl_2 at -78°C gives $[\{\text{Co}(\text{CO})_4\}_2\text{PPh}]$ (1) in good yield. A solution of (1) evolves CO gas at 60°C giving $[\text{Co}_2(\text{CO})_7(\text{PPh})]$. Complex (1) reacts with $[\text{Fe}_2(\text{CO})_9]$ to form a new mixed-metal cluster complex $[\text{Co}_2\text{Fe}(\text{CO})_9(\text{PPh})]$.

THE formation of cobalt carbonyl clusters of general formula $[\text{Co}_3(\text{CO})_9\text{E}]$ (E = a main-group or transition element plus ligands to satisfy its electronic requirements) from $\text{Na}[\text{Co}(\text{CO})_4]$ or $[\text{Co}_2(\text{CO})_8]$ and various trihalide compounds, *e.g.* PX_3S ,¹ PX_3 ,¹ or AlCl_3 ,² has been reported. Also, the possibility of building the cluster from dihalide reagents such as PRCl_2 to give $[\text{Co}_3(\text{CO})_9(\text{PR})]$ (R = Ph, Bu^t , or NEt_2) has been described.³ No mechanism of formation of these latter complexes has been suggested although it seems feasible that an intermediate species $[\{\text{Co}(\text{CO})_4\}_2\text{PR}]$ is involved. We now report an investigation of the reaction of $\text{Na}[\text{Co}(\text{CO})_4]$ and PPhCl_2 and the isolation of a new type of phosphine complex.

RESULTS AND DISCUSSION

In recent years the group PPh^4 has been shown to be capable of several different modes of co-ordination to transition metals, due to variations in the use of its four available electrons; Huttner *et al.*^{5,6} have been concerned with preparing phosphinediyl complexes. An X-ray crystal-structure determination⁵ of $[\{\text{Mn}(\text{cp})(\text{CO})_2\}_2\text{PPh}]$ (cp = $\eta\text{-C}_5\text{H}_5$) shows that the formally electron-deficient phosphorus atom has a trigonal planar arrangement of

ligands, and is stabilised by metal(d_π)-phosphorus(p_π) bonding [see (A)]. A more common mode of bonding



for the PPh ligand is triply bridging metal atoms as in $[\text{Fe}_3(\text{CO})_9(\text{PPh})_2]$.⁷ Another example³ is the series of paramagnetic complexes $[\text{Co}_3(\text{CO})_9(\text{PR})]$ (R = Ph, Bu^t , or NEt_2). The latter complexes are believed to contain a tetrahedral Co_3P arrangement [see (B)]. A third mode

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† Part 11, B. Stutte, V. Bätzel, R. Boese, and G. Schmid, *Chem. Ber.*, 1978, **111**, 1603.

¹ A. Vizi-Orosz, G. Pályi, and L. Markó, *J. Organometallic Chem.*, 1973, **60**, C25.

² K. E. Schwarzshans and H. Steiger, *Angew. Chem.*, 1972, **84**, 587.

³ L. Markó and B. Markó, *Inorg. Chim. Acta*, 1975, **14**, L39.

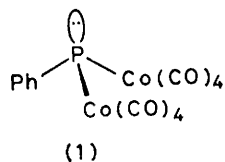
⁴ K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307.

⁵ G. Huttner, H. D. Müller, A. Frank, and H. Lorenz, *Angew. Chem.*, 1975, **87**, 714.

⁶ G. Huttner, G. Mohr, and A. Frank, *Angew. Chem.*, 1976, **88**, 719.

⁷ P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, 1972, **11**, 1609.

of bonding was encountered⁸ in the tetracobalt cluster complex $[\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2(\mu\text{-PPh})_2]$. Determination of the structure by X-ray diffraction methods shows the phosphorus atoms to be five-co-ordinate, each PPh group bridging four cobalt atoms [see (C)].



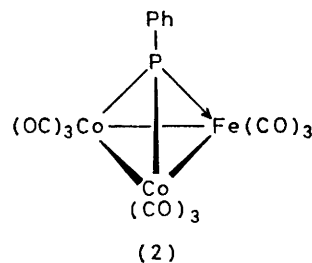
We have prepared the complex $[\{\text{Co}(\text{CO})_4\}_2\text{PPh}]$ (1) which demonstrates a fourth mode of bonding of the PPh group to transition metals. The complex is formed in the reaction of PPhCl_2 with $\text{Na}[\text{Co}(\text{CO})_4]$ at -78°C as a red-orange solid which is stable at room temperature and very soluble in toluene, but insoluble in hexane. The i.r. spectrum shows a simple pattern in the terminal carbonyl-stretching region, indicative of $\text{Co}(\text{CO})_4$ groups, and no bridging-carbonyl bands. Further absorptions are characteristic of a phenyl group. The elemental analysis supports the formation given. A structure for (1) is proposed containing two independent $\text{Co}(\text{CO})_4$ groups bridged by the PPh ligand.

The reaction of (1) with $[\text{Fe}_2(\text{CO})_9]$ was found to give the diamagnetic mixed-metal cluster $[\text{Co}_2\text{Fe}(\text{CO})_9(\text{PPh})]$ (2) as black, moderately air-stable, crystals. The i.r. spectrum of (2) in the carbonyl-stretching region shows six bands, none indicative of bridging carbonyl groups. The pattern is similar to that quoted for the analogous complex $[\text{Co}_2\text{Fe}(\text{CO})_9\text{S}]$;⁹ however, the frequencies are shifted towards lower values in accordance with the higher basicity of the PPh group compared to that of sulphur. This effect has been noticed³ before in the i.r. spectra of the complexes $[\text{Co}_3(\text{CO})_9\text{X}]$ [$\text{X} = \text{PR}$,³ compared to S^{10} or CR' (ref. 11)]. The mass spectrum of (2) shows a parent ion at m/e 534, and peaks for successive loss of five to nine carbonyl groups. A high-resolution mass spectrum confirms that the molecule is $[\text{Co}_2\text{Fe}(\text{CO})_9(\text{PPh})]$ (Found: m/e 533.767 35. $^{12}\text{C}_{15}\text{H}_5^{59}\text{Co}_2^{56}\text{Fe}^{16}\text{O}_9^{31}\text{P}$ requires 533.769 81. Found: 534.769 81. $^{12}\text{C}_{15}\text{H}_5^{59}\text{Co}_2^{57}\text{Fe}^{16}\text{O}_9^{31}\text{P}$ requires 534.768 89).

The structure of $[\text{Co}_2\text{Fe}(\text{CO})_9\text{S}]$ has been determined by X-ray crystallography.¹² The complex consists of a basal $\text{M}_3(\text{CO})_9$ fragment symmetrically linked to the apical sulphur atom. This basal fragment is composed of three $\text{M}(\text{CO})_3$ groups identically positioned at the vertices of an equilateral triangle with the metals joined to one another by direct metal-metal interactions and by the triply bridging sulphur atom. We propose that the structure of (2) is analogous to that of $[\text{Co}_2\text{Fe}(\text{CO})_9\text{S}]$, likewise containing an equilateral triangular arrangement of the Co_2Fe atoms bonded symmetrically to the apical PPh

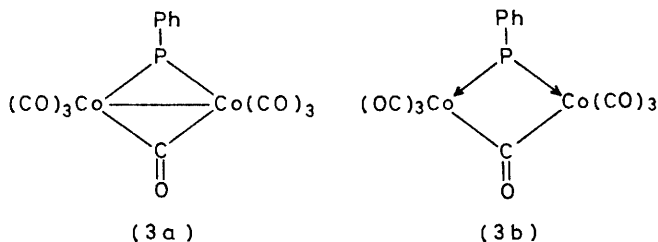
group. The PPh group acts formally as a four-electron donor.

The effect of an unpaired electron on the structure and stability towards air of these cluster complexes has already been discussed.^{12,13} Comparison¹² of the structures of paramagnetic $[\text{Co}_3(\text{CO})_9\text{S}]$ and diamagnetic $[\text{Co}_2\text{Fe}(\text{CO})_9\text{S}]$ shows that the metal-metal bond lengths in the latter complex are on average nearly 0.1 Å shorter. This is accounted for by accommodation of the unpaired electron of $[\text{Co}_3(\text{CO})_9\text{S}]$ in a molecular orbital which is antibonding with respect to the metal-metal bonds. The unpaired electron is also believed⁹ to cause the observed high sensitivity to air, whereas $[\text{Co}_2\text{Fe}(\text{CO})_9\text{S}]$ is stable to oxidation. Similarly, crystals of paramagnetic $[\text{Co}_3(\text{CO})_9(\text{PPh})]$ are sensitive to air, but (2) is moderately stable for short periods.



A second product was isolated during the reaction of (1) with $[\text{Fe}_2(\text{CO})_9]$ and identified as $[\text{Co}_2(\text{CO})_7(\text{PPh})]$ (3). This was shown to be a thermal-decomposition product of (1) and best prepared by heating a solution of (1) at 60°C . To optimise the yield of the cluster (2) it was therefore necessary to keep the temperature of the reaction of (1) with $[\text{Fe}_2(\text{CO})_9]$ below 55°C .

The i.r. spectrum of (3) shows four bands in the carbonyl-stretching region. The single band at 1879 cm^{-1} is indicative of a bridging carbonyl group. A structure (3a) may be suggested in which a carbonyl group and the PPh ligand bridge the two cobalt atoms. To satisfy the electronic requirements of the cobalt atoms a metal-metal bond is assumed. This structure is formally derived from $[\text{Co}_2(\text{CO})_8]$ by replacement of one CO bridge by PPh. The carbonyl stretching frequencies are correspondingly lowered compared to $[\text{Co}_2(\text{CO})_8]$.



EXPERIMENTAL

Microanalyses were by the A. Bernhardt Mikroanalytisches Laboratorium, Elbach. Infrared spectra were recorded on

¹¹ G. Bor, L. Markó, and B. Markó, *Chem. Ber.*, 1962, **95**, 333.

⁸ R. C. Ryan and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6904.

⁹ S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometallic Chem.*, 1964, **1**, 373.

¹⁰ L. Markó, G. Bor, and E. Klumpp, *Chem. and Ind.*, 1961, 1491.

¹² D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6027.

¹³ C. E. Strouse, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6032.

a Perkin-Elmer 457 spectrometer and calibrated using polystyrene. The Fourier-transform ^{31}P n.m.r. spectrum was obtained on a Varian XL 100 spectrometer, using H_3PO_4 as external standard. The mass spectrum of (2) was obtained on a Varian CH7 machine.

All the operations were carried out under an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen by distilling over potassium (toluene) or $\text{Li}[\text{AlH}_4]$ (diethyl ether, benzene, or light petroleum). Samples of PPhCl_2 , $[\text{Co}_2(\text{CO})_8]$, and $[\text{Fe}_2(\text{CO})_9]$ were obtained commercially. The salt $\text{Na}[\text{Co}(\text{CO})_4]$ was prepared according to the literature method.¹⁴

Reactions.— $\text{Na}[\text{Co}(\text{CO})_4]$ with PPhCl_2 . A toluene solution (10 cm^3) of PPhCl_2 (0.724 g, 4.04 mmol) was added dropwise to a suspension of $\text{Na}[\text{Co}(\text{CO})_4]$ (1.57 g, 8.09 mmol) in toluene (40 cm^3) containing diethyl ether (2 cm^3) at -78°C . The mixture was stirred for 2 h at -78°C and then allowed to warm slowly to room temperature. The red reaction mixture was filtered and the filtrate added dropwise to light petroleum (250 cm^3), resulting in immediate precipitation of an orange solid. This was recrystallised from toluene–light petroleum giving μ -phenylphosphinediyl-bis(tetracarbonylcobalt) (1), 950 mg (52%), m.p. 95°C (decomp.) (Found: C, 37.05; H, 1.35; Co, 26.2; P, 7.15. Calc. for $\text{C}_{14}\text{H}_5\text{Co}_2\text{O}_8\text{P}$: C, 37.35; H, 1.10; Co, 26.2; P, 6.90%); $\nu(\text{CO})$ at 2 072m, 2 020vs, and 1 995 (sh) cm^{-1} in Nujol.

* Throughout this paper: 1 mmHg $\approx 13.6 \times 9.8$ Pa.

¹⁴ W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, 1958, **B13**, 192.

Complex (1) with $[\text{Fe}_2(\text{CO})_9]$. Diethyl ether (5 cm^3) and $[\text{Fe}_2(\text{CO})_9]$ (180 mg, 0.49 mmol) were added to a stirred toluene solution (30 cm^3) of (1) (170 mg, 0.38 mmol) at room temperature. The mixture was stirred at 45°C for 4 h and then at 50°C for 30 min. The resulting solution was filtered and the solvent removed *in vacuo*. Pentacarbonyliron was removed from the residue at 0.1 mmHg * which was then extracted by stirring overnight with light petroleum (40 cm^3). Solvent was removed from the extract and a black solid sublimed out of the residue at 80°C (0.05 mmHg). Recrystallisation from light petroleum gave black needles of 1,1,1,2,2,2,3,3,3-nonacarbonyl- μ_3 -phenylphosphinediyl-triangulo-dicobaltiron (2), 5 mg (2.5%) (Found: C, 33.6; H, 1.10%; M 534. Calc. for $\text{C}_{15}\text{H}_5\text{Co}_2\text{FeO}_9\text{P}$: C, 33.7; H, 0.95%; M 534); $\nu(\text{CO})$ at 2 101w, 2 059vs, 2 048vs, 2 039vs, 1 981w, and 1 969w cm^{-1} in light petroleum.

Thermal Decomposition of Complex (1).—A stirred toluene solution (30 cm^3) of (1) (200 mg, 0.44 mmol) was heated at 60°C for 5 h. The resulting solution was filtered and solvent removed *in vacuo*. The light petroleum-soluble part of the residue was chromatographed on silica gel. An orange-red band was eluted with toluene–light petroleum (1:10) and solvent removed leaving a red solid. Recrystallisation from benzene gave red crystalline μ -carbonyl- μ -phenylphosphinediyl-bis(tricarbonylcobalt) (Co–Co) (3), 15 mg (8%), m.p. 256 – 258°C (Found: C, 36.85; H, 1.35; Co, 27.8. Calc. for $\text{C}_{13}\text{H}_5\text{Co}_2\text{O}_7\text{P}$: C, 36.95; H, 1.20; Co, 27.95%); $\nu(\text{CO})$ at 2 048vs, 2 039vs, 2 023vs, and 1 879m cm^{-1} in light petroleum.

[7/1982 Received, 10th November, 1977]