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Preliminary communication

THE REACTION OF $Co_4(CO)_{12}$ WITH $Ph_2PCH_2CH_2PPh_2$. SPECTROSCOPIC IDENTIFICATION OF POLYMERIC PRODUCTS

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Summary

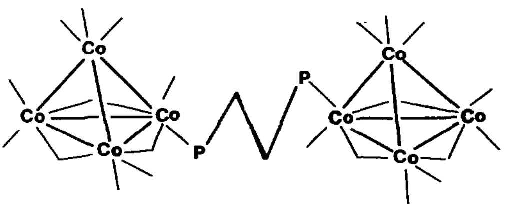
$Co_4(CO)_{12}$ readily undergoes replacement of CO by 1,1-bis(diphenylphosphino)ethane (DPPE) and several derivatives have been characterized. In addition to $\{[Co_4(CO)_{11}]_2(\mu\text{-DPPE})\}$ (I) and $[Co_4(CO)_{10}(DPPE)]$ (II), two polymeric products have been identified by IR and ^{31}P NMR spectroscopy. The ^{13}C and ^{31}P variable temperature NMR spectra of I and II are reported.

Replacement of the CO ligands of $Co_4(CO)_{12}$ by Group V donor ligands occurs readily, as was early shown by Cetini [1] and Poilblanc [2]. Under mild conditions up to four CO groups can be replaced by $P(OMe)_3$ [2], but ligands of higher basicity, such as PPh_3, give only the monosubstituted product before extensive breakdown of the cluster takes place [1].

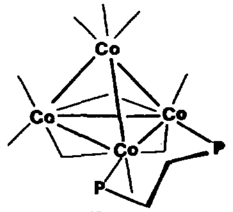
More recently, Darensbourg, following a detailed investigation of ligand substitution processes in tetranuclear carbonyl clusters [3], reported that the reaction between $Co_4(CO)_{12}$ and $HC(PPh_2)_3$ (tripod) gives only the $[Co_4(CO)_9(\text{tripod})]$ complex [4]; no other substituted product containing more cluster units trapped by the tripod ligand were observed.

These observations prompted us to present some preliminary results obtained for the reaction between $Co_4(CO)_{12}$ and DPPE.

The reaction of $Co_4(CO)_{12}$ (1 mmol) and DPPE (2 mmol) in n-hexane takes place almost instantaneously at room temperature, as indicated by the disappearance of the IR absorption due to $Co_4(CO)_{12}$, TLC work-up (SiO_2; eluent, petroleum ether/Et_2O 9/1) affords two brown products whose spectral data correspond to I and II [5], respectively.



(I)



(II)

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The IR spectrum of I is completely consistent with that previously reported for monosubstituted Co$_4$(CO)$_{11}$L species, and a dimeric structure (with one DPPE ligand bridging two Co$_4$(Co)$_{11}$ clusters) is unambiguously indicated by the single ^{31}P resonance in the region of coordinated phosphorus ligands.

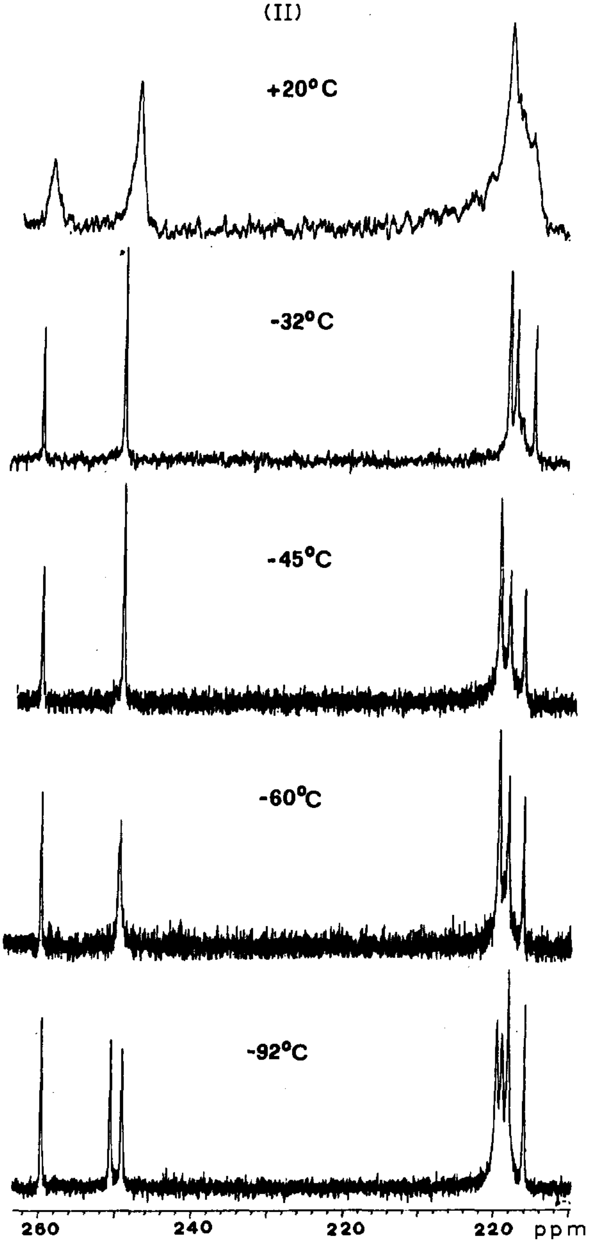

Fig. 1. ^{13}C VT-NMR spectra of Co(CO)$_{10}$(DPPE) (II) at 67.9 MHz in CD$_2$Cl$_2$; the sample was enriched with ^{13}CO at ~10% level.

The ^{13}C variable temperature (VT) NMR spectra of I, in the carbonyl region, parallel those reported by Brown and coworkers [6] for $[Co_4(CO)_{11}P(OPh)_3]$, but the higher magnetic field used in our work allowed the observation of all the expected resonances. Furthermore, the larger molecular dimension of I results in an increase in the molecular correlation time which leads to shortening of t_1 for the quadrupolar cobalt nuclei: this in turn allows a significant sharpening of resonances in the low temperature spectra of the CO groups bonded to the apical cobalt atom

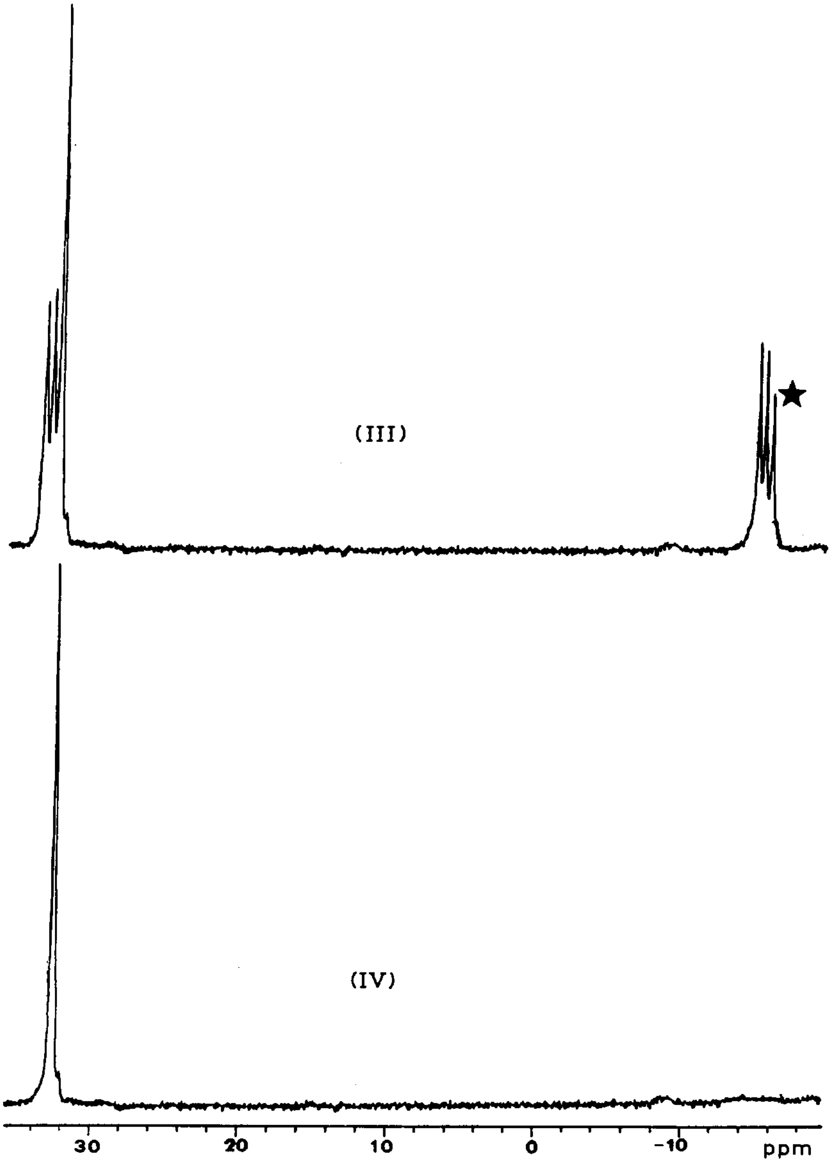

Fig. 2. ^{31}P NMR spectra of IIIa and IVb recorded at 106.9 MHz in $CDCl_3$ (−30 °C). The signal marked with an asterisk is from a small quantity of free DPPE.

[7]. At −92°C, the lowest field μ_2-CO bridging resonance of intensity 2 is quite broad as is the ^{31}P resonance at the same temperature: this behaviour is indicative of a slowing of the localized axial–radial exchange of the coordinated phosphorus atoms. (This process is better defined for complex II, vide infra.) Use of DPPE, a ligand with a flexible "bite", has previously given related dimeric compounds, namely $\{[Ru_3(CO)_{11}]_2(\mu\text{-DPPE})\}$ [8], $\{[PhCCo_3(CO)_8]_2(\mu\text{-DPPE})\}$ [9] and $\{[H_4Ru_4(CO)_{11}]_2(\mu\text{-DPPE})\}$ [10].

The ^{13}C VT NMR spectra of II are shown in Fig. 1. As can be seen, the DPPE ligand introduces stereochemical rigidity into the carbonyl frame compared with that of the parent $Co_4(CO)_{12}$ molecule, and the broadening of the ^{13}C resonances observed in the spectra at +25°C is probably the result of relaxation effects induced by the quadrupolar ^{59}Co nuclei rather than of an incipient exchange process. On the other hand the P atoms of the DPPE ligand are involved in a mutual axial–radial exchange which can be frozen out only at low temperatures: this process ($\Delta G^{\star}$ 9.3 kcal/mol) is umambiguously defined from the splitting of the ^{13}CO resonances centered at 249.6 and 199.3 ppm (as measured at −45°C) and from the broadening of the ^{31}P signal in their low temperature limiting spectra. In this derivative the resonances from the CO ligands bonded to the apical cobalt are not observed, probably because their broad absorption overlap with the narrowly spaced set from the terminally bonded carbonyls.

An alternative possibility for II would be a double bridged dimeric structure $[Co_4(CO)_{10}(\mu\text{-DPPE})]_2$, but the steric constraint results from the close proximity of the two DPPE ligands bridging the $Co_4(CO)_{10}$ moieties renders this unlikely.

The yields of I and II (~20% for both together) are markedly lower than expected on the basis of the results obtained with other phosphito and phosphine ligands. However, extraction with $CHCl_3$ of a brown band from the baseline of the TLC plates allows the isolation in low yield of a further product (III), whose IR spectrum in $CHCl_3$ is almost identical to that of II. On the other hand, its ^{31}P NMR spectrum (Fig. 2) differs markedly from II, since it shows a singlet of intensity two at 29.9 ppm and two doublets (^3J(PP) 49.5 Hz) of relative intensity one at 30.6 and −17.7 ppm, respectively; the high field doublet can be readily assigned to non-coordinated phosphorus atoms of two "dangling" DPPE molecules whose other phosphorus atoms (which give rise to the low field doublet) are coordinated to the Co_4 clusters.

The addition of solutions of $Co_4(CO)_{12}$ in $CDCl_3$ directly to the solution in the NMR tube leads to the disappearance of the two doublets in the ^{31}P NMR spectrum (Fig. 2) and, interestingly, the IR spectrum of the solution now shows a pattern corresponding to the superposition of I and II in the relative intensity ratio of 2/3. From these observations we think that a trimeric linear structure can be assigned to III; the addition of $Co_4(CO)_{12}$ converts it into IV by complete coordination of the terminal phosphorus atoms to the added Co_4-units.

$$P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P$$

(III)

$$-2CO \Big\downarrow +2\,Co_4(CO)_{12}$$

$$(CO)_{11}Co_4\text{-}P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P\text{-}Co_4(CO)_{10}\text{-}P\frown P\text{-}Co_4(CO)_{11}$$

(IV)

This easy interconversion between polymeric clusters bridged by the flexible bidentate DPPE is probably due to the high affinity of $Co_4(CO)_{12}$ molecules towards Group V donor ligands [1,2]. The main features of the results were confirmed when a reaction between $Co_4(CO)_{12}$ and DPPE was carried out directly in the NMR tube and monitored by ^{31}P NMR spectroscopy. Even at $-30°C$ (solvent $CDCl_3$, 1/2 molar ratio between $Co_4(CO)_{12}$ and DPPE) the reaction proceeds quite readily to give III as the major product (~ 60%) and I and II in a combined yield of ca. 15% [11]. Other experiments involving different $Co_4(CO)_{12}$/DPPE ratios gave results in complete agreement with the observations reported above: higher $Co_4(CO)_{12}$/DPPE molar ratios afford higher yields of I and IV; lower ratios favour II, III. When a solution of III and IV is placed on SiO_2-plates, extensive decomposition takes place, and brown bands corresponding to I and II then start to be eluted.

Moderate heating of n-hexane solution of these complex mixtures (40°C, 15 min) does not lead to drastic modifications in the ratios of the various components, although somewhat more pronounced effects were observed in polar media. The partial decomposition of the polymeric species to afford the isolable complexes I and II thus seems to be associated with interaction with the silica of the TLC plates.

The variety of coordination modes to transition metal clusters shown by DPPE merits comment. This ligand may chelate the same metal atom or bridge a metal–metal bond [12] (with possible isomerism arising from the coordination of phosphorus atoms at equatorial or axial sites), or link two cluster units.

A comparison of the behaviour of various di- and tri-phosphine ligands towards $Co_4(CO)_{12}$ and other polymetallic substrates is in progress.

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5 Selected spectroscopic data:
I: IR (ν(CO) (cm^{-1}), n-hexane) 2084(s), 2048(vs), 2042(vs), 2031(s), 2001(m), 1987(m), 1852(m) and 1831(m). $^{31}P\{^1H\}$NMR (106.9 MHz, CD_2Cl_2, +20°C); 44.0 ppm. (positive downfield from H_3PO_4 85%). ^{13}C NMR (67.8 MHz, CD_2Cl_2, −92°C), CO region: 248.8(2), 244.7(1), 200.1(1), 198.7(3, broad), 196.0(2) and 193.9(2) ppm. Anal. Found: C, 38.55, H, 1.83; Co, 31.97. $C_{48}H_{24}O_{22}P_2Co_8$ calcd.: C, 38.76; H, 1.61; Co, 31.76%.
II: IR (ν(CO) (cm^{-1}), n-hexane), 2070(vs), 2026(vs), 2020(vs), 1988(br), 1876(w), 1838(m). $^{31}P\{^1H\}$ NMR (106.9 MHz, CD_2Cl_2, −92°C): 46.3(1) and 39.3(1) ppm (from H_3PO_4 85%). ^{13}C NMR (67.8 MHz, CD_2Cl_2, −92°C), CO region: 259.7(1), 250.6(1), 249.1(1), 199.6(1), 199.0(1), 198.2(1) and 196.1(1) ppm. Anal. Found: C, 47.17; H, 2.53; Co 26.06. $C_{36}H_{24}O_{10}P_2Co_4$ calcd.: C, 47.26; H, 2.63; Co, 25.82%.

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