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COMPLEXES OF THE TRIPOD LIGAND, TRIS(DIPHENYLPHOSPHINO)METHANE

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Summary

Tris(diphenylphosphino)methane (TPM) is shown to exhibit a variety of coordination modes. In [Fe(CO)$_4$(TPM)] and [Mo(CO)$_5$(TPM)] it is monodentate while in [Fe(CO)$_3$(TPM)] and *cis*-[Mo(CO)$_4$(TPM)], two of the three phosphorus atoms chelate to the metal. The uncoordinated arms of TPM in the mono- and bidentate complexes can coordinate other metals to give the homo- and heterobimetallic complexes [(OC)$_4$Fe(μ-TPM)Fe(CO)$_3$], [(OC)$_4$Fe(μ-TPM)Mo(CO)$_4$] and *trans*-[RhCl(CO)(*cis*-Mo(CO)$_4$(TPM))$_2$]. In the last, an unusual virtually-coupled ^{31}P NMR spectrum is seen. With [RCCo$_3$(CO)$_9$] (R = H, Cl) under mild conditions is formed [RCCo$_3$(CO)$_7$(TPM)] in which the ligand functions in a bidentate, bridging fashion while under more strenuous conditions the ligand-capped clusters [RCCo$_3$(CO)$_6$(TPM)] form.

Introduction

Considerable interest has been shown in recent years in the use of metal clusters as potential homogeneous catalysts [1]. A recurring problem in these studies has been to provide a convincing demonstration that the actual catalysis occurs on an intact cluster rather than on mononuclear fragments generated under reaction conditions. One possible means of circumventing the problem of fragmentation is to stabilize the cluster by coordinating a ligand which can bridge the metal atoms. A very popular ligand in binuclear systems has been bis(diphenylphosphino)methane (DPM) and the ligand-stabilized dimers it forms show a range of interesting chemistry [2–6]. However, for the study of cluster catalysis it would be desirable to have ligand-stabilized clusters containing at least three metal atoms, particularly if such species are to be considered as homogeneous models for reactions occurring on metal surfaces [7]. An attractive ligand is tris(diphenylphosphino)methane (TPM) [8] which appeared suitable for capping a trinuclear array of metal atoms. At the time this work was initiated, the only species of this type which had been reported was

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[MeSi(PBu$^n_3$)$_3$Ru$_3$(CO)$_9$] [9] however in the interim reports have appeared on the synthesis of [Ru$_3$(CO)$_9$(TPM)] [10], the rearrangement product [Ru$_3$(CO)$_9$-(HC(PPh$_2$)(PhPC$_6$H$_4$PPh))] [10], [Ni$_3$(CO)$_6$(TPM)] [11], the capped tetramers [M$_4$(CO)$_9$(TPM)] (M = Co, Rh, Ir) [12] and a rearrangement product, [Ir$_3$(CO)$_6$-(Ph)(μ_3-PPh)(μ-DPM)], formed in an alternate synthesis of [Ir$_4$(CO)$_9$(TPM)] [13]. We report here on our initial studies of the ligand behavior of TPM.

Experimental

All solvents were appropriately dried and distilled prior to use and all manipulations were carried out in an atmosphere of prepurified nitrogen using standard Schlenk techniques. Tris(diphenylphosphino)methane, pentacarbonyliron, nonacarbonyldiiron, dodecacarbonyltriiron, and hexacarbonylmolybdenum were purchased from Strem Chemicals while literature methods were used to prepare [RhCl(CO)$_2$]$_2$ [14], [RhCl(COD)]$_2$ [15] (COD = cycloocta-1,5-diene), [Mo(CO)$_5$(pip)] [16], *cis*-[Mo(CO)$_4$(pip)$_2$] [16] (pip = piperidine) and [RCCo$_3$(CO)$_9$] [17] (R = H, Cl). Infrared spectra were obtained on Perkin–Elmer Models 298 and 683 spectrophotometers. Proton NMR spectra were obtained on a Varian Associates EM-390 spectrometer at 90 MHz using tetramethylsilane (0.0 ppm) as an internal standard. Phosphorus-31 and carbon-13 NMR spectra were obtained on a JEOL FX-60 spectrometer at 24.15 and 15.03 MHz respectively using the pulsed-fourier transform method with noise decoupling and a flip angle of 45°. Pulse repetition rates were 5 and 30 sec. respectively. Phosphorus chemical shifts are referred to external 85% phosphoric acid (0.0 ppm) while carbon chemical shifts are referred to external tetramethylsilane (0.0 ppm) and both are positive downfield. Elemental analyses and molecular weight determination were provided by Galbraith Laboratories, Knoxville, Tennessee.

[Fe(CO)$_4$(HC(PPh$_2$)$_3$)]. A mixture of 0.86 g (1.512 mmol) of HC(PPh$_2$)$_3$ and 0.55 g (1.512 mmol) of [Fe$_2$(CO)$_9$] were stirred under reflux in 35 ml of tetrahydrofuran for 2.5 h. The solvent was evaporated under reduced pressure and the residue dissolved in dichloromethane. Addition of heptane followed by removal of the dichloromethane under reduced pressure precipitated some unreacted ligand which was removed by filtration. Further concentration of the filtrate afforded the product as large red-orange crystals (0.67 g, 60%). Anal. Found: C, 66.7; H, 4.4. $C_{41}H_{31}O_4P_3Fe$ calcd. C, 66.87; H, 4.24%.

[Fe(CO)$_3$(HC(PPh$_2$)$_3$)]. A mixture of [Fe$_2$(CO)$_9$] (2.0 g, 5.5 mmol) and pyridine (8 ml) was stirred in 35 ml of tetrahydrofuran under carbon monoxide for 3 h at room temperature. To the resulting solution was added 2.5 g (4.4 mmol) of HC(PPh$_2$)$_3$ dissolved in 15 ml of tetrahydrofuran and the mixture was refluxed for 3 h under nitrogen. The solvent was stripped off and the residue was recrystallized twice from dichloromethane/heptane containing 10% n-butanol to give the product as yellow crystals in 60% yield. Anal. Found: C, 67.3; H, 4.7; P, 13.5. $C_{40}H_{31}O_3P_3Fe$ calcd.: C, 67.81; H, 4.41; P, 13.12%.

cis-[Mo(CO)$_4$(HC(PPh$_2$)$_3$)]. Equimolar quantities of *cis*-[Mo(CO)$_4$(pip)$_2$] and HC(PPh$_2$)$_3$ were stirred briefly in dichloromethane solution. The product was precipitated by addition of diethyl ether and recrystallized from dichloromethane/diethyl ether, in virtually quantitative yield, as pale yellow needles. The complex can also be prepared directly from the ligand and a three-fold excess of $[Mo(CO)_6]$ in refluxing tetrahydrofuran (40 h reaction time, 60% yield). In this instance, the reaction solution was filtered and evaporated to dryness under reduced pressure. The residue was washed with n-butanol and recrystallized from dichloromethane/heptane. Anal. Found: C, 63.4; H, 4.1. $C_{41}H_{31}O_4P_3Mo$ calcd.: C, 63.41; H, 4.02%.

$[Fe(CO)_4(cis\text{-}Mo(CO)_4(HC(PPh_2)_3))]$. Equimolar quantities of $[Fe(CO)_4(HC(PPh_2)_3)]$ and *cis*-$[Mo(CO)_4(pip)_2]$ were heated in dichloromethane solution for 15 min. Addition of methanol to the cooled solution precipitated *cis*-$[Mo(CO)_4(HC(PPh_2)_3)]$ which was filtered off. Slow evaporation of the filtrate yielded yellow-orange crystals of the product in ca. 40% yield. Anal. Found: C, 57.2; H, 3.4. $C_{45}H_{31}O_8P_3FeMo$ calcd.: C, 57.22; H, 3.32%.

trans-$\{RhCl(CO)($*cis*-$Mo(CO)_4(HC(PPh_2)_3))_2\}$. Carbon monoxide was bubbled through a toluene solution of $[RhCl(COD)]_2$ (0.067 g, 0.135 mmol) for 30 min followed by addition of *cis*-$[Mo(CO)_4(HC(PPh_2)_3)]$ (0.420 g, 0.540 mmol) dissolved in toluene. The yellow solution which resulted was purged with nitrogen and then stirred under reduced pressure for several minutes. Addition of diethyl ether and hexane until the solution became cloudy precipitated a small quantity of a yellow powder which was removed by filtration. The filtrate was left to stand overnight whereupon the product formed as yellow crystals (0.3 g, 60%). These appeared air-stable but decomposed on attempted recrystallization. The complex can also be prepared from $[RhCl(CO)_2]_2$ in benzene but it proved extremely difficult to obtain a crystalline product by this route. Anal. Found: C, 57.2; H, 3.6; Cl, 2.2. $C_{83}H_{62}O_9P_6ClMoRh$ calcd.: C, 57.97; H, 3.64; Cl, 2.06%.

$[Fe_2(CO)_7(HC(PPh_2)_3)]$. Equimolar quantities of $HC(PPh_2)_3$ and freshly sublimed $[Fe_3(CO)_{12}]$ were dissolved in toluene and stirred at 70°C for 2.5 h. The cooled reaction mixture was filtered and diluted with heptane. After standing for 24 h, the mother liquor together with an amorphous precipitate was removed from the flask by decantation. The brownish yellow crystalline product adhering to the walls of the flask was washed with heptane, scraped free and dried in vacuo (yield ca. 30%). Anal. $C_{44}H_{31}O_7P_3Fe_2$ calcd.: C, 60.31; H, 3.57%; *M*, 876.36. Found: C, 60.0; H, 3.8; *M*, 570.

$[RCCo_3(CO)_7(HC(PPh_2)_3)]$ ($R = H$, Cl). Equimolar quantities of $HC(PPh_2)_3$ and $[RCCo_3(CO)_9]$ were stirred for 96 h ($R = H$) or 48 h ($R = Cl$) in 40 ml of toluene at 25°C. The reaction mixture was taken to dryness under reduced pressure and the residue extracted with toluene (10 ml) and filtered. The product was precipitated with heptane and recrystallized from toluene/heptane as green-black crystals in 30% yield. Anal. ($R = H$) Found: C, 56.4; H, 3.7; P, 10.2. $C_{45}H_{32}O_7P_3Co_3$ calcd.: C, 56.63; H, 3.38; P, 9.74%.

$[RCCo_3(CO)_6(HC(PPh_2)_3)]$ ($R = H$, Cl). Toluene solutions of $[RCCo_3(CO)_7(HC(PPh_2)_3)]$ or of equimolar quantities of $HC(PPh_2)_3$ and $[RCCo_3(CO)_9]$ were heated at 70°C with stirring for 12 h. For $R = H$ addition of heptane produced a precipitate which was discarded. The remaining solution was taken to dryness under reduced pressure and the residue crystallized from dichloromethane/heptane to yield fluffy red microcrystals in 30% yield. Anal. Found: C, 57.7; H, 3.8; P, 10.7. $C_{44}H_{32}O_6P_3Co_3$ calcd.: C, 57.04; H, 3.48; P, 10.03%. For $R = Cl$, a fibrous red precipitate formed on dilution of the reaction mixture with heptane. This was collected, washed with ethanol until the washings were colorless and was recrystal-

lized from toluene/heptane (yield 70%). Anal. Found: C, 55.2; H, 3.5; P, 9.7. $C_{44}H_{31}O_6P_3Co_3Cl$ calcd.: C, 55.00; H, 3.25; P, 9.67%.

Results and discussion

With the hope of forming trinuclear complexes capped by the TPM ligand we initially carried out reactions of TPM with various carbonyl complexes of molybdenum, iron and rhodium using a metal/ligand ratio of at least 3/1. In no case were we able to promote the assemblage of a TPM-capped cluster as has been reported for nickel [11] and iridium [13]. Even when $[Fe_3(CO)_{12}]$ was used fragmentation occurred in the course of the reaction. The majority of complexes initially isolated contained either monodentate or bidentate TPM and particularly in the iron systems mixtures of complexes were formed. Subsequently we have developed directed syntheses of the complexes identified in these initial studies and they will be discussed first. Infrared and $^{31}P\{^1H\}$ NMR spectroscopic data are presented in Table 1.

The reaction of $[Fe_2(CO)_9]$ with TPM in refluxing tetrahydrofuran affords the first example of a monodentate TPM complex formulated as $[Fe(CO)_4(TPM)]$ (**1**). The ^{31}P NMR spectrum clearly shows the presence of coordinated and uncoordinated phosphorus atoms in a 1/2 ratio. The appearance of the spectrum is

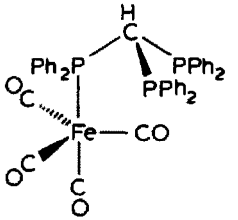
TABLE 1

SPECTROSCOPIC DATA

Complex	$\nu(CO)$ (cm^{-1}) [a,b]	$\delta(^{31}P)$ (ppm) [c]
$[Fe(CO)_4(TPM)]$ (**1**)	2043s, 1970m, 1948vs, 1919s	−4.7, 79.2 (AA'X) (^2J(P–P) 78.0, 88.1 Hz)
$[Mo(CO)_5(TPM)]$ (**2**)		−9.4, 43.6 (AA'X) (^2J(P–P) 112.8, 124.1 Hz)
$[Fe(CO)_3(TPM)]$ (**3**)	1985vs, 1919s, 1908s	−20.3(t), 30.2(d) (^2J(P–P) 15.2 Hz)
$[Mo(CO)_4(TPM)]$ (**4**)	2022s, 1920vs, 1905vs, 1869vs [d]	−23.5(t), 20.4(d) (^2J(P–P) 29.5 Hz)
$[Fe(CO)_4(Mo(CO)_4(TPM))]$ (**5**)	2048s, 2018s, 1978m, 1945vs, 1924vs, 1900vs [e]	46.4(d), 80.5(t) (^2J(P–P) 14.6 Hz)
$[RhCl(CO)(Mo(CO)_4(TPM))_2]$ (**6**)	2021s, 1983s, 1928vs, 1907vs, 1890vs	33.8("t"), 41.1("dq") (^1J(Rh–P) 125.1, ^2J(P–P 350, J(P–P') 4.9 Hz)
$[Fe_2(CO)_7(TPM)]$ (**7**)	2049s, 1989vs, 1974m, 1946vs, 1924vs, 1912sh	61.6(d), 74.1(t) (^2J(P–P 18.1 Hz)
$[HCCo_3(CO)_7(TPM)]$ (**8**)	2054s, 2004vs, 1987sh, 1966sh [e]	~ −1.9(t), 64.5(d), 60.6(d) (^2J(P–P) 16.2, 18.5 Hz)
$[ClCCo_3(CO)_7(TPM)]$ (**9**)	2062s, 2015vs, 1999sh, 1978sh	5.7(t), 60.2(d) (^2J(P–P) 18.0 Hz)
$[HCCo_3(CO)_6(TPM)]$ (**10**)	2024m, 1994s, 1957w	44.4(s)
$[ClCCo_3(CO)_6(TPM)]$ (**11**)	2030m, 1999s, 1965w	46.0(s)
TPM		−10.4(s)

[a] Key: vs, very strong; s, strong; m, medium; w, weak. [b] THF solution unless otherwise specified. [c] Key: s, singlet; d, doublet; t, triplet; "t", apparent triplet; "dq" apparent doublet of quintets. [d] Nujol mull. [e] CH_2Cl_2 solution.

somewhat solvent-dependent with the most informative being that obtained in dichloromethane. No change is seen on cooling to −78°C apart from a slight viscosity-broadening. The appearance of both resonances as apparent doublets of doublets implies at minimum a magnetic nonequivalence of the uncoordinated phosphorus atoms. Simulation [18,19] as either an AA′X or an ABX spin system gave about equally satisfactory results and although marginally better agreement was obtained with the latter this may be simply the result of having more variable parameters. While it is therefore not possible to say with certainty whether or not there is any chemical shift difference between the uncoordinated phosphorus atoms, it is clear that they are unequally coupled to the coordinated phosphorus atom suggesting that at least there is some difference in the P–C–P angles involving the latter. The infrared spectrum of **1** in the carbonyl region shows four absorptions. While this could be taken to indicate equatorial coordination of TPM [22], well-characterized examples of $[Fe(CO)_4L]$ (L = phosphine, phosphite) complexes show the phosphorus ligand to favor axial coordination. We therefore prefer the latter

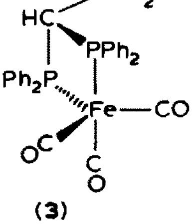


(1)

structure and suggest that the four band patterns results from a splitting of the E mode presumably because of the asymmetric nature of the TPM ligand. Similar four band patterns have been previously found for the axially-substituted complexes $[Fe(CO)_4(P(OMe)_3)]$ and $[Ph(EtO)CFe(CO)_4]$ [22]. The $^{13}C\{^1H\}$ NMR spectrum of **1** in the carbonyl region is a doublet at δ 214.8 (^2J(P–C) 17.1 Hz) which compares favorably with that found for $[Fe(CO)_4(PPh_3)]$ [23] and indicates a rapid interconversion of axial and equatorial carbonyl groups.

No reaction is observed to occur between TPM and $[Mo(CO)_5(pip)]$ at room temperature while in refluxing dichloromethane the only isolable product is the chelated derivative *cis*-$[Mo(CO)_4(TPM)]$ (vide infra). However in situ monitoring of the reaction by ^{31}P NMR showed that after about 15 min at reflux traces of a species were present whose spectrum (Table 1) is analogous to that described above for **1** and which could be similarly analyzed. On this basis we tentatively formulate this species as the monodentate complex $[Mo(CO)_5(TPM)]$ (**2**).

The chelate complexes $[Fe(CO)_3(TPM)]$ (**3**) and *cis*-$[Mo(CO)_4(TPM)]$ (**4**) are



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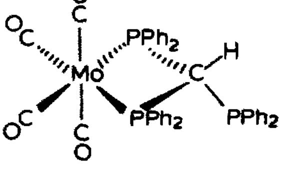
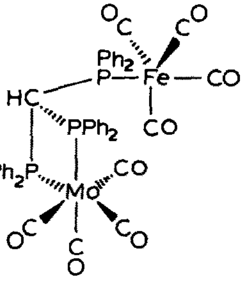


(4)

readily formed from [Fe(CO)$_4$(py)] (prepared in situ) and *cis*-[Mo(CO)$_4$(pip)$_2$] respectively. The infrared spectra in the carbonyl region compare well with those reported previously for [Fe(CO)$_3$(L$_2$)] (L$_2$ = bis(diphenylphosphino)methane (DPM), 1,2-bis(diphenylphosphino)ethane) [24] and for a variety of *cis*-[Mo(CO)$_4$L$_2$] (L = phosphine or phosphite) complexes [16]. The ^{31}P NMR spectra (Table 1) clearly show the presence of coordinated and uncoordinated phosphorus atoms, now in a 2/1 ratio, with the expected AX$_2$ splitting patterns. The chemical shifts and coupling constants compare favorably with those reported for [Ni(CO)$_2$(TPM)] [11] and [M(CO)$_4$(TPM)] (M = Cr, W) [25]. The structure of **3** with axial-equatorial coordination of the ligand is presumed by analogy with that found for [Fe(CO)$_3$(DPM)] [25]. The ^{31}P NMR spectrum of **3** remains a simple AX$_2$ pattern to − 80°C indicating that it, like [Fe(CO)$_3$(DPM)] [24], is undergoing a rapid intramolecular exchange of phosphorus nuclei. The fluxionality is also indicated by the observation that the ^{13}C{^{1}H} NMR spectrum in the carbonyl region consists of one triplet resonance at δ 220.6 (^2J(P–C) 6.8 Hz) which compares favorably with that found for [Fe(CO)$_3$(Me$_2$PCH$_2$CH$_2$PMe$_2$)] [27].

To explore the coordinating abilities of the free arm(s) of the TPM ligand in **1**, **3** and **4** and in the hope of preparing mixed-metal clusters stabilized by this ligand we investigated the reactions of these complexes with several species containing readily replaceable ligands. Complex **1** readily reacts with *cis*-[Mo(CO)$_4$(pip)$_2$] to yield [Fe(CO)$_4$(*cis*-Mo(CO)$_4$(TPM))] (**5**). The infrared spectrum in the carbonyl region is virtually a superimposition of those of **1** and **4** while the ^{31}P NMR spectrum shows the presence of only coordinated phosphorus atoms. From the relative intensities (low field/high field = 1/2) and the splitting pattern, the lower field resonance can be assigned to the phosphorus coordinated to iron. The ^{13}C NMR spectrum in the carbonyl region shows a doublet at δ 214.0 (^2J(P–C) 15.6 Hz) which is virtually identical to that observed in **1**. This is assigned to the {Fe(CO)$_4$} moiety and again indicates the fluxionality of this unit. Additional resonances, presumably due to the {Mo(CO)$_4$} moiety were observed to lower field but because of the extremely poor signal-to-noise ratio here, a reliable interpretation could not be made. To determine if the {Mo(CO)$_4$} moiety had the expected [28] splitting pattern when bound to TPM we attempted to obtain the ^{13}C NMR spectrum of **4** but again were frustrated by a very poor signal-to-noise ration. Presumably a combination of the considerable splitting of the ^{13}C resonances by the phosphine and the unfavorable relaxation time for the carbonyl carbon atoms on molybdenum are responsible for the extremely weak signal. A similar problem has been noted in attempts to obtain the ^{13}C NMR spectrum of *cis*-[Mo(CO)$_4$(DPM)] [28]. Despite our failure to obtain the ^{13}C NMR



(**5**)

spectrum for the $\{Mo(CO)_4\}$ moiety in **5** the remaining spectroscopic data adequately support the proposed formulation.

A second heterobimetallic complex was initially detected as a product of the reaction of **4** with $[RhCl(CO)_2]_2$. In situ monitoring of the reaction by ^{31}P NMR showed the presence of new signals of low intensity downfield of those due to unreacted **4** with the lowest field resonance showing rhodium–phosphorus coupling. Under ambient conditions the reaction appears to proceed only to a limited extent, however on refluxing the solution under a nitrogen purge, more complete conversion occurred. Unfortunately, the ^{31}P NMR spectrum of the final solution showed the presence of unidentified impurities in addition to the expected product and only with difficulty could a tractable solid be obtained. We suspect that the geometrical constraints of the TPM ligand in **4** render its ability to cleave the $[RhCl(CO)_2]_2$ dimer rather difficult. Considerably greater success in preparing a rhodium complex of **4** was realized by initially cleaving $[RhCl(COD)]_2$ with carbon monoxide before adding **4**. The resulting complex, **6**, is formulated as *trans*-$[RhCl(CO)($*cis*-$Mo(CO)_4(TPM))_2]$ on the basis of its analytical and spectroscopic data. Thus the infrared spectrum shows an additional carbonyl absorption which is very similar to that found for a wide variety of complexes $[RhCl(CO)L_2]$ (L = phosphine, arsine) [29]. Of particular note is the ^{31}P NMR spectrum (Fig. 1) which clearly shows the presence of only coordinated phosphorus atoms. The large primary splitting of the lowfield resonance as well as the relative intensity indicates that this is the phosphorus coordinated to rhodium while the further splitting can only be reproduced if the remaining four phosphorus atoms are considered to be equivalently coupled to the first pair. This can be rationalized with the assumption that "virtual" coupling occurs and this in turn supports the assignment of *trans* geometry about rhodium.

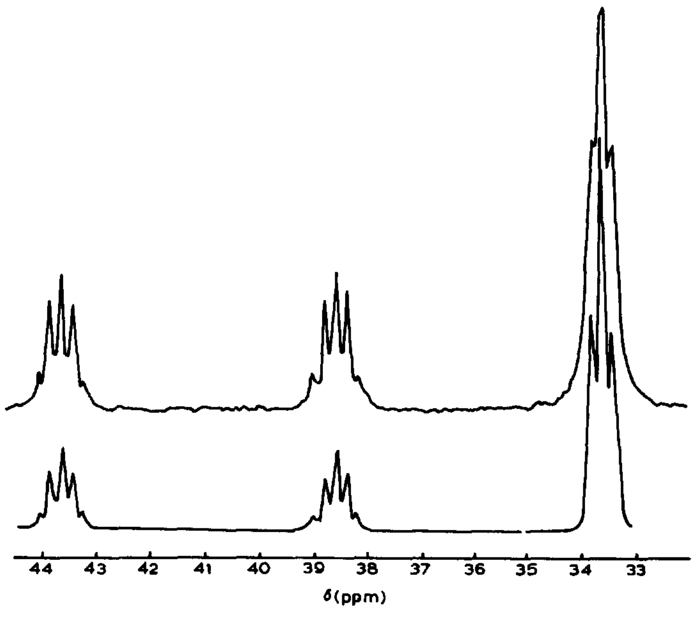
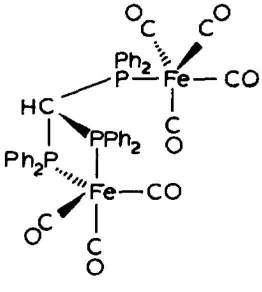


Fig. 1. Observed and calculated $^{31}P\{^1H\}$ NMR spectra of *trans*-$[RhCl(CO)($*cis*-$Mo(CO)_4(TPM))_2]$ in C_6D_6 at 28°C.

To the best of our knowledge, this is the first observation of the effects of "virtual" coupling in the ^{31}P NMR spectrum of a coordinated phosphine. Although $^2J(P-P)$ across the rhodium is not directly observable, the value listed in Table 1 enabled the spectrum to be satisfactorily simulated [18] and is in the range previously observed in related complexes of rhodium(I) [30]. We also attempted the reaction of **3** with $[Mo(CO)_5(pip)]$ but no attachment of a $\{Mo(CO)_5\}$ moiety to the free arm of the TPM ligand could be detected by ^{31}P NMR spectroscopy. This result was somewhat surprising in light of the successful preparation of **5** and **6**. However it is likely that access to the free arm of TPM which is already chelated to a metal is quite restricted as is indicated by the reluctance to react with $[RhCl(CO)_2]_2$ and it may be that the $\{Mo(CO)_5\}$ moiety is too bulky to coordinate effectively. Conversely, the monodentate TPM ligand in **1** should be more flexible and therefore more able to coordinate one of the free arms to a second metal. Also, the opportunity to then chelate to this center should provide a driving force for the formation of a stable bimetallic complex.

In a final attempt to obtain a TPM-stabilized trimetallic cluster, the ligand was reacted with $[Rh(CO)_2Cl_2]^-$. Evolution of carbon monoxide was observed to occur and an extremely insoluble yellow powder showing a single carbonyl absorption at 1998 cm^{-1} soon formed. A dilute solution in dimethylsulfoxide showed ill-defined resonances attributable to coordinated phosphorus together with one which could be assigned to uncoordinated phosphorus. However the solution appeared to be unstable so the NMR results are inconclusive. Although it appears that at best a binuclear species was formed, the intractability of the system has prevented adequate characterization of the species formed.

In none of the systems described above have we been able to generate a TPM-stabilized complex in which two or more metal atoms could be expected to be in close proximity. Attempts to effect partial decarbonylation of the bimetallic complexes by thermal or photochemical means so as to promote closer association of the metal atoms led only to decomposition or to recovery of unreacted starting material. We therefore turned our attention to the reaction of TPM with preformed trinuclear clusters. Unlike the reaction with $[Ru_3(CO)_{12}]$ [10] the reaction of TPM with $[Fe_3(CO)_{12}]$ does not yield a ligand-capped trinuclear complex. The complex obtained from freshly-sublimed $[Fe_3(CO)_{12}]$ analyzes as $[Fe_2(CO)_7(TPM)]$ (**7**) and shows an infrared spectrum which is virtually a superimposition of those of **1** and **3**. The ^{31}P NMR spectrum shows two resonances attributable to only coordinated phosphorus atoms and having an intensity ratio of 2/1 (doublet and triplet respectively). The ^{13}C NMR spectrum shows a doublet at δ 213.7 ($^2J(P-C)$ 17.1 Hz) and a poorly resolved apparent triplet at δ 219.4. While not having a very satisfactory signal-to-noise ratio, the spectrum nevertheless appears to be a superimposition of those found for **1** and **3**. The measured molecular weight (vapor pressure osmometry in THF) is markedly lower than expected for the formula suggested by the above data. However, solutions of **7** appear to be rather air-sensitive and we attribute this discrepancy to some decomposition which occurred during the measurement. Despite this we feel the molecular weight data are more consistent with the formulation $[Fe_2(CO)_7(TPM)]$ for **7** than with a formulation of higher molecular complexity (vide infra). Thus the most likely structure for **7** is a TPM-bridged one analogous to that proposed for **5**. While we have not studied the formation of **7** in detail, we speculate that it may involve initial coordination of the TPM ligand in a bridging fashion across the base of the iron triangle. This could be followed by loss of the unsubstituted vertex and coordination of the third arm of the ligand to one of the two remaining iron atoms.



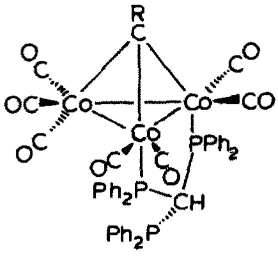
(7)

In our initial attempts to use TPM to assemble a triiron cluster using an excess of iron carbonyl complexes ([Fe(CO)$_5$], [Fe(CO)$_4$(py)], [Fe$_2$(CO)$_9$] or commercial [Fe$_3$(CO)$_{12}$] (contains methanol)) under thermal or photochemical conditions we invariably found that considerable decomposition occurred and mixtures of **1**, **3** and **7** were obtained. The same results were found when **1** was reacted with either [Fe$_2$(CO)$_9$] or [Fe$_3$(CO)$_{12}$]. Since it appears that no species having more than two iron atoms per TPM ligand are formed in these reactions, the amorphous solids formed in the initial reactions presumably result from decomposition of the excess iron carbonyls used.

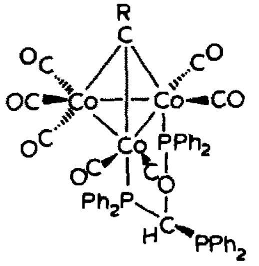
Fragmentation of the TPM ligand also appears to occur in the reaction with the commercial [Fe$_3$(CO)$_{12}$] where methanol is present as evidenced by the formation of a small amount of a complex identified as [Fe$_2$(CO)$_4$(μ-CO)(DPM)$_2$] [31,32]. Confirmation of this species as a complex of DPM was obtained by its independent synthesis from [Fe$_3$(CO)$_{12}$] and DPM.

Considerably greater success in obtaining a trinuclear complex capped by TPM was achieved in the reaction of the ligand with the alkylidynenonacarbonyltricobalt complexes [RCCo$_3$(CO)$_9$] (R = H, Cl). At room temperature, the ligand binds as a bidentate, bridging ligand to give [RCCo$_3$(CO)$_7$(TPM)] (R = H (**8**), Cl (**9**)). The infrared spectra are comparable to other bis(phosphine) derivatives of these clusters [33] and the mode of coordination of the ligand is confirmed by the ^{31}P NMR spectra. The reported spectra were obtained at −80°C to minimize the extensive quadrupolar broadening of the coordinated phosphorus resonances that occurs at room temperature. The ^{31}P NMR spectrum of **8** shows the presence of two isomers in which the free arm of the ligand appears as two nearly coincident triplet resonances while the coordinated portion is seen as two well-separated doublet resonances (Table 1). No evidence of interconversion of these was seen at or below room temperature. Possible structures of these isomers are **8a**–**8c** with the first and last being preferred.

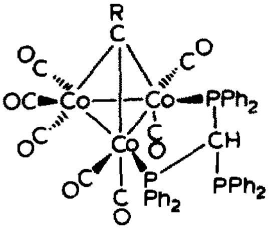
On heating, **8** and **9** are converted into **10** and **11**, respectively, which show the presence of only coordinated phosphorus atoms in their ^{31}P NMR spectra (at −80°C). The single resonance indicates they should be formulated as [RCCo$_3$(CO)$_6$(TPM)] with the cobalt triangle capped by the TPM ligand. This has been confirmed by a determination of the structure of **11** [34]. Complexes **10** and **11** appear to be more robust than their unsubstituted precursors. Presumably this could



(8a)

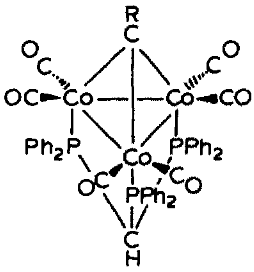


(8b)



(8c)

extend the range of the chemistry which could be carried out on the alkylidyne moiety although we have not pursued this as our current interest is in reactions which may be able to be carried out on the face of the tricobalt moiety. Therefore we



10 (R = H)
11 (R = Cl)

have attempted to remove the alkylidyne moiety but so far have met with little success. Under mild conditions, **11** can be converted to **10** on treatment with hydride sources such as borohydride or triethylborohydride ions while, under more strenuous conditions, further reaction appears to occur as evidenced by loss of the original carbonyl absorptions but no characterizable products could be isolated. Similar behavior was noted where lithium aluminum hydride was used. Also **10** and **11** and could be recovered unchanged when treated with 25 psi of hydrogen at 60°C in tetrahydrofuran for 24 h.

Finally, some comments on the ^{31}P chemical shifts in the complexes reported here are warranted. It has been proposed that the mode of coordination (chelating vs. bridging) of multidentate phosphine ligands can be determined from the ^{31}P chemical shifts [35]. In particular the formation of a four-membered chelate ring with DPM results in a considerable upfield shift when compared to what is observed when the ligand is monodentate or bridging two metals. There have however been recent suggestions that this rule is not universally applicable [36]. From Table 1 it appears that this upfield "ring contribution" occurs in **3** and **4** since the chemical shifts of the coordinated phosphorus atoms are much further upfield than those of the single coordinated phosphorus atom in **1** and **2**. An analogous result is seen in comparing [Fe(CO)$_4$(DPM)] with [Fe(CO)$_3$(DPM)] where the coordinated phosphorus atoms are found at 74.5 and 19.4 ppm respectively [24]. While it is risky to compare chemical shifts between complexes of different metals, the significant downfield shift of the coordinated phosphorus atoms in the cobalt complexes **8** and

9 is consistent with the ligand bridging two metals as proposed. Since it is suggested that the "ring contribution" is additive, the observation that the phosphorus chemical shift occurs at higher field in the capped clusters **10** and **11** further supports this conclusion.

The situation becomes less clear when one considers the bimetallic complexes **5**–**7**. Since there is little doubt that the TPM ligand is still chelated to molybdenum in **5** and **6** it is evident that coordination of a second metal to the third arm of the ligand causes a downfield shift of the chelated phosphorus atoms of 26 and 13 ppm respectively as compared to what is observed in **4**. Since in comparing **5** with **4** the effect of the attachment of a $\{Fe(CO)_4\}$ moiety to the TPM ligand in **4** results in a 26 ppm downfield shift of the phosphorus atoms chelated to molybdenum it is reasonable to assume that the effect of attaching this same moiety to the TPM ligand in **3** would be a downfield shift of comparable magnitude for the phosphorus atoms chelated to the $\{Fe(CO)_3\}$ moiety. We therefore feel that the ^{31}P NMR data for **7** are consistent with the structure proposed since the downfield shift of the phosphorus atoms assigned as chelating to the $\{Fe(CO)_3\}$ moiety (31.4 ppm relative to **3**) is not substantially greater than we see in a situation where chelation of one end of the TPM ligand can be confidently assumed to occur. While the doublet resonance at 61.6 ppm is also consistent with this end of the TPM ligand bridging two iron atoms since $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}DPM)]$ [37] and $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}DPM)_2]$ [31] show phosphorus resonances at 60.6 and 67.7 ppm respectively, for **7** to have a similar structure would require it to be formulated as $[Fe_4(CO)_{13\text{ or }14}(TPM)_2]$ in order to fit the observed elemental analysis. Even though the molecular weight data are not particularly convincing, they are considerably less consistent with this formulation than with that proposed. Also both of the DPM-bridged dimers also contain one bridging carbonyl ligand and if a similar structure for **7** were to be correct we would expect to see a bridging carbonyl there too while in fact no evidence for one exists. Thus we feel that our proposed formulation for **7** is the most reasonable one.

Because the number of complexes of TPM is relatively limited at present, it is premature to attempt a detailed discussion of the correlation of its phosphorus chemical shifts with possible modes of coordination. However it appears at the moment that considerable caution should be exercised in attempting to determine the mode of coordination on the basis of phosphorus chemical shift alone.

Conclusions

Tris(diphenylphosphino)methane has been found to function as a monodentate, a bidentate, or a tridentate ligand. Its ability to function as a template for the formation of trinuclear clusters does not appear to be a general property. While it seems to stabilize alkylidynetricobalt clusters, the resulting species do not appear to be useful precursors to reactive ligand-stabilized tricobalt clusters.

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