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η^1, η^2 -Hetero-bimetallic phospho-alkyne complexes. Synthesis and NMR spectra of $[\text{Pt}(\text{dppe})(^t\text{BuCP})\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

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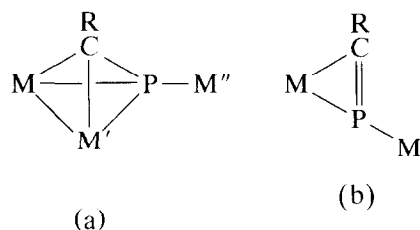
Abstract

Hetero-bimetallic complexes of the type $[\text{Pt}(\text{dppe})(^t\text{BuCP})\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), containing an η^1, η^2 -ligated phospho-alkyne, are reported.

1. Introduction

There is considerable interest in the coordination chemistry of phosphorus compounds having low coordination numbers [1–3]. Coordination complexes of the phospho-alkyne ligand $\text{RC}\equiv\text{P}$ ($\text{R} = ^t\text{Bu}$) (type (a)), involving both η^2 - and η^1 -ligating behaviour, have been made previously by certain tri- and poly-metallic systems, *e.g.*, $[\text{Co}_2(\text{CO})_6(^t\text{BuCP})\text{W}(\text{CO})_5]$ [4], $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(^t\text{BuCP})\text{W}(\text{CO})_5]$ [5], $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(^t\text{BuCP})\text{Os}_3(\text{CO})_{11}]$ [6], $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(^t\text{BuCP})\text{W}(\text{CO})_5]$ [7], $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(^t\text{BuCP})\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ [7], *trans*- $[\text{PtCl}_2(\text{PR}_3)\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(^t\text{BuCP})]$ ($\text{PR}_3 = \text{Bu}_3, \text{PEt}_3, \text{PPh}_2\text{Me}, \text{PPr}_3$) [8], *trans*- $[\text{PdCl}_2(\text{PBu}_3)\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(^t\text{BuCP})]$ [8] and *trans*- $[\text{RhCl}(\text{PF}_2\text{NMe})_2\text{Co}]\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(^t\text{BuCP})]$ [8]. A second type of η^1, η^2 -phospho-alkyne complexation to two different metals exemplified by type (b) has not previously been described, although oligomers of the type $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(^t\text{BuCP})]_n$ ($\text{M} = \text{Ti}, n = 2; \text{M} = \text{Zr}, n = 3$) and $[\text{Pd}_2\text{Pt}_3(^t\text{BuCP})_3(\text{PPh}_3)_5]$ involving this bonding mode to the same metal are known [9,10]. We now report the

synthesis and detailed NMR spectroscopic study of bimetallic phospho-alkyne complexes containing zero-valent platinum(0) and Group VIA transition metals having structure (b).



2. Results and discussion

Treatment of $[\text{Pt}(\text{dppe})(^t\text{BuCP})]$ [11] (**1**) with an excess of freshly prepared $[\text{Cr}(\text{CO})_5\text{THF}]$ in tetrahydrofuran (THF) solution at room temperature readily gave a high yield of the yellow microcrystalline complex $[\text{Pt}(\text{dppe})(^t\text{BuCP})\text{Cr}(\text{CO})_5]$ (**2**), whose formulation was confirmed by elemental analysis, and its structure established as type (b) by IR and ^{31}P NMR spectroscopy (*vide infra*). The IR spectrum of **2** in CH_2Cl_2 solution shows four $\nu(\text{CO})$ bands, at 2056, 1978, 1940, and 1929 cm^{-1} , typical for the presence of the $[\text{Cr}(\text{CO})_5]$ fragment [12] and similar to those observed previously for related diphosphene complexes [13,14] and established for $[\text{Pd}(\text{dppe})(\text{PhP}=\text{PPh})\text{W}(\text{CO})_5]$, whose structure

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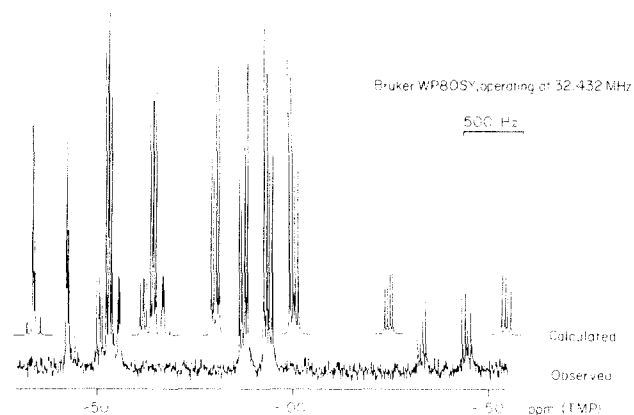


Fig. 1. Observed and calculated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for $[\text{Pt}(\text{dppe})(\eta^2\text{-}^1\text{BuC}\equiv\text{P})]$ (**1**).

has been determined by a single crystal X-ray diffraction study [13].

Complex **2** was also formed when $[\text{Pt}(\text{dppe})(^1\text{BuCP})]$ was treated with an excess of $[\text{Cr}(\text{CO})_4\text{NBD}]$ (NBD = norbornadiene) in tetrahydrofuran. Analogous reactions, carried out with $[\text{Pt}(\text{dppe})(^1\text{BuCP})]$ and $[\text{Mo}(\text{CO})_5\text{THF}]$ or $[\text{W}(\text{CO})_5\text{THF}]$ in tetrahydrofuran at room temperature, gave dark red crystals of the complexes $[\text{Pt}(\text{dppe})(^1\text{BuCP})\text{Mo}(\text{CO})_5]$ (**3**) and $[\text{Pt}(\text{dppe})(^1\text{BuCP})\text{W}(\text{CO})_5]$ (**4**), respectively, in high yield. The formulation of **3** and **4** is supported by elemental analysis and their structures are judged to be similar to **2** on the basis of IR and ^{31}P NMR spectroscopic data. The IR spectrum of **3** shows the expected four $\nu(\text{CO})$ bands in CH_2Cl_2 at 2088, 1977, 1945, and 1925 cm^{-1} , while **4** exhibits bands at 2046, 1981, 1953, and 1925 cm^{-1} .

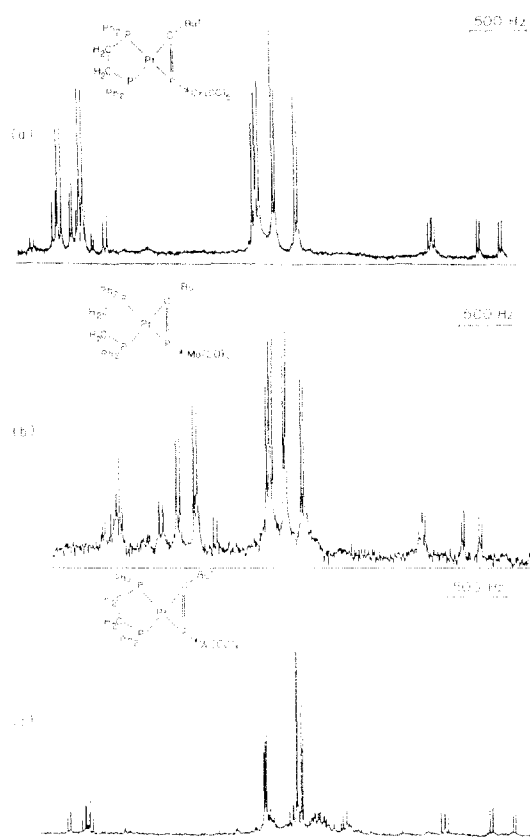


Fig. 2.

2.1. ^{31}P NMR spectra

The ^{31}P NMR spectrum of $[\text{Pt}(\text{dppe})(^1\text{BuCP})]$ (**1**) is shown in Fig. 1, and those of $[\text{Pt}(\text{dppe})(^1\text{BuCP})\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}$ (**2**), Mo (**3**), W (**4**)) in Fig. 2(a)–(c). A full analysis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}(\text{dppe})(^1\text{BuCP})]$ affords the following chemical shift and cou-

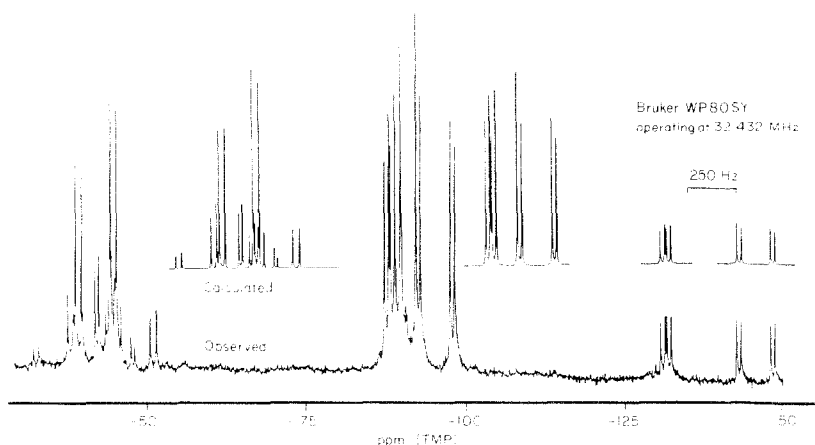
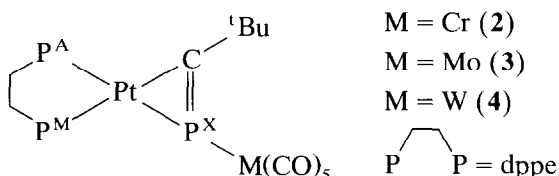


Fig. 3. Observed and calculated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for $[\text{Pt}(\text{dppe})(\eta^2\text{-}^1\text{BuC}\equiv\text{P}) \rightarrow \text{Cr}(\text{CO})_5]$ (**2**).

pling constant data *: $\delta_{P(A)}$ 43.5; $\delta_{P(M)}$ 47.4; $\delta_{P(X)}$ 87.9 ppm. $^1J_{PtP(A)} + 2946$; $^1J_{PtP(M)} + 3294$; $^1J_{PtP(X)} - 169$; $^2J_{P(A)P(M)} 46.2$; $^2J_{P(M)P(X)} \pm 21.0$; $^2J_{P(A)P(X)} \mp 28.1$ Hz.

Similarly, analysis of the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(dppe)(^tBuCP)Cr(CO)_5]$ (**2**) afforded: $\delta_{P(A)}$ 46.1; $\delta_{P(M)}$ 53.1; $\delta_{P(X)}$ 99.0 ppm. $^1J_{PtP(A)} + 3299$; $^1J_{PtP(M)} + 28.29$; $^1J_{PtP(X)} + 395.6$; $^2J_{P(A)P(M)} \pm 22.6$; $^2J_{P(A)P(X)} \pm 177.5$; $^2J_{P(M)P(X)} \mp 31.9$ Hz.

The simulated spectra are shown in Fig. 1 and 3, respectively. The progressive change in the chemical shift $\delta_{P(X)}$ in the complexes in going from Cr to Mo to W ($\delta_{P(X)}$ 99.0 (Cr); 76.6 (Mo); 46.3 (W) ppm), is exactly that expected on the basis of extensive ^{31}P NMR studies on tertiary phosphane complexes of Group VI metal carbonyls [15]. This strongly supports a structure of type (b), in which the $[M(CO)_5]$ fragment is coordinated to tBuCP via the phosphorus lone pair.



3. Experimental details

3.1. Preparation of $[Pt(dppe)(^tBuCP)Cr(CO)_5]$ (**2**)

A two-fold excess of $[Cr(CO)_5THF]$ was prepared in THF solution (100 cm³) from $[Cr(CO)_6]$ (0.127 g, 0.577 mmol). $[Pt(dppe)(^tBuCP)]$ (0.20 g, 0.288 mmol) was added, and the mixture was stirred for 2 h, during which the colour changed from orange to pale yellow. After removal of solvent, the resulting yellowish solid was washed several times with petroleum ether (60–80°C), to give the yellow microcrystalline complex $\{[1,2-bis-(diphenylphosphino)ethane-P,P]\{2,2-dimethylpropyldynephosphine-P',C\}-platinum(0)]-P-pentacarbonylchromium(0)\}$ (0.234 g, 89%). Anal. Found: C, 48.3; H, 3.65. $C_{36}H_{33}O_5P_3CrPt$ calc.: C, 48.28; H, 3.76%.

Complex **2** was also obtained when a solution of $[Pt(dppe)(^tBuCP)]$ (0.160 g, 0.231 mmol) in THF solution (15 cm³) was treated with an excess of $[Cr(CO)_4NBD]$ (NBD = norbornadiene) (0.080 g, 0.312 mmol). The mixture was stirred for 12 h at room temperature, during which the colour changed from bright yellow to pale yellow. The solvent was pumped to dryness and the product (0.123 g, 60%) washed several times with petroleum ether (60–80°C).

* Carried out by Dr. D. Carmichael. A full paper, including signs of coupling constants in these and related diphosphene, phospho-alkene, and phospho-allene complexes, will be the subject of a future publication.

3.2. Preparation of $[Pt(dppe)(^tBuCP)Mo(CO)_5]$ (**3**)

Similarly, a two-fold excess of $[Mo(CO)_6THF]$ prepared from $[Mo(CO)_6]$ (0.152 g, 0.577 mmol) in THF solution (100 cm³) was treated with $[Pt(dppe)(^tBuCP)]$ (0.20 g, 0.288 mmol) to afford the dark red crystalline complex $\{[1,2-bis-(diphenylphosphino)ethane-P,P]\{2,2-dimethylpropyldynephosphine-P',C\}-platinum(0)]-P'-pentacarbonyl-molybdenum(0)\}$ (0.255 g, 92.4%). Anal. Found: C, 46.3; H, 3.5. $C_{36}H_{33}O_5P_3MoPt$ calc.: C, 46.51; H, 3.58%.

Complex **3** (0.215 g, 89%) was also obtained from $[Pt(dppe)(^tBuCP)]$ (0.180 g, 0.259 mmol) and an excess of $[Mo(CO)_4NBD]$ (0.10 g, 0.333 mmol) in THF solution (20 cm³).

3.3. Preparation of $[Pt(dppe)(^tBuCP)W(CO)_5]$ (**4**)

In an identical procedure to that described above, a two-fold excess of $[W(CO)_5THF]$, prepared from $[W(CO)_6]$ (0.263 g, 0.577 mmol) in THF solution (100 cm³), was treated with $[Pt(dppe)(^tBuCP)]$ (0.20 g, 0.288 mmol), to give the brownish microcrystalline complex $\{[1,2-bis-(diphenylphosphino)ethane-P,P]\{2,2-dimethylpropyldynephosphine-P',C\}-platinum(0)]-pentacarbonyltungsten(0)\}$ (0.270 g, 89.6%). Anal. Found: C, 42.0; H, 3.2. $C_{36}H_{33}O_5P_3PtW$ calc.: C, 42.50; H, 3.27%.

Complex **4** (0.210 g, 71%) was also obtained by treating $[Pt(dppe)(^tBuCP)]$ (0.20 g, 0.288 mmol) with an excess of $[W(CO)_4NBD]$ (0.150 g, 0.385 mmol) in THF solution (15 cm³).

Acknowledgements

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