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

Duncan Carmichael [1], Saud I. Al-Resayes [2] and John F. Nixon
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (UK)

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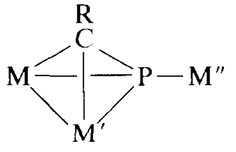
Abstract

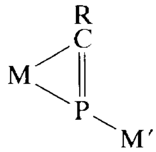
Hetero-bimetallic complexes of the type [Pt(dppe)(^{t}BuCP)M(CO)$_5$] (M = Cr, Mo, W), containing an η^1,η^2-ligated phospha-alkyne, are reported.

1. Introduction

There is considerable interest in the coordination chemistry of phosphorus compounds having low coordination numbers [1–3]. Coordination complexes of the phospha-alkyne ligand RC≡P (R = ^{t}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.*, [Co$_2$(CO)$_6$(^{t}BuCP)W(CO)$_5$] [4], [Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$(^{t}BuCP)W(CO)$_5$] [5], [Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$(^{t}BuCP)Os$_3$(CO)$_{11}$] [6], [CoNi(η^5-C$_5$H$_5$)(CO)$_3$(^{t}BuCP)W(CO)$_5$] [7], [CoNi(η^5-C$_5$H$_5$) (CO)$_3$ (^{t}BuCP) Mn(η^5-C$_5$H$_5$) (CO)$_2$] [7], *trans*-[PtCl$_2$(PR$_3$)Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$(^{t}BuCP)] (PR$_3$ = Bu$_3$, PEt$_3$, PPh$_2$Me, PPr$_3$) [8], *trans*-[PdCl$_2$(PBu$_3$)Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$(^{t}BuCP)] [8] and *trans*-[RhCl{(PF$_2$NMe)$_2$CO}Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$ (^{t}BuCP)] [8]. A second type of η^1,η^2-phospha-alkyne complexation to two different metals exemplified by type (b) has not previously been described, although oligomers of the type [M(η^5-C$_5$H$_5$)$_2$(^{t}BuCP)]$_n$ (M = Ti, n = 2; M = Zr, n = 3) and [Pd$_2$Pt$_3$(^{t}BuCP)$_3$(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 phospha-alkyne complexes containing zerovalent platinum(0) and Group VIA transition metals having structure (b).



(a)



(b)

2. Results and discussion

Treatment of [Pt(dppe)(^{t}BuCP)] [11] (**1**) with an excess of freshly prepared [Cr(CO)$_5$THF] in tetrahydrofuran (THF) solution at room temperature readily gave a high yield of the yellow microcrystalline complex [Pt(dppe)(^{t}BuCP)Cr(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$_2$Cl$_2$ solution shows four ν(CO) bands, at 2056, 1978, 1940, and 1929 cm^{-1}, typical for the presence of the [Cr(CO)$_5$] fragment [12] and similar to those observed previously for related diphosphene complexes [13,14] and established for [Pd(dppe){(PhP=PPh)[W(CO)$_5$]$_2$}], whose structure

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Correspondence to: Professor J.F. Nixon.

[1] Present address: DCPH, Ecole Polytechnique, F-91128, Palaiseau, France.

[2] Present address: Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia.

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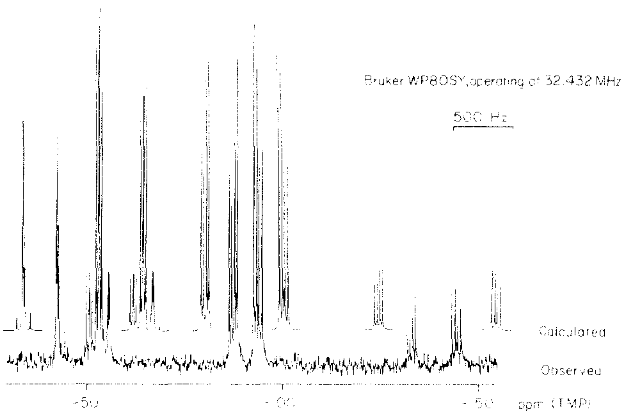


Fig. 1. Observed and calculated $^{31}P\{^1H\}$ NMR spectra for [Pt(dppe)(η^2-^{t}BuC≡P)] (1).

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

Complex **2** was also formed when [Pt(dppe)(^{t}BuCP)] was treated with an excess of [Cr(CO)$_4$NBD] (NBD = norbornadiene) in tetrahydrofuran. Analogous reactions, carried out with [Pt(dppe)(^{t}BuCP)] and [Mo(CO)$_5$THF] or [W(CO)$_5$THF] in tetrahydrofuran at room temperature, gave dark red crystals of the complexes [Pt(dppe)(^{t}BuCP)Mo(CO)$_5$] (**3**) and [Pt(dppe)(^{t}BuCP)W(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 ν(CO) bands in CH$_2$Cl$_2$ at 2088, 1977, 1945, and 1925 cm^{-1}, while **4** exhibits bands at 2046, 1981, 1953, and 1925 cm^{-1}.

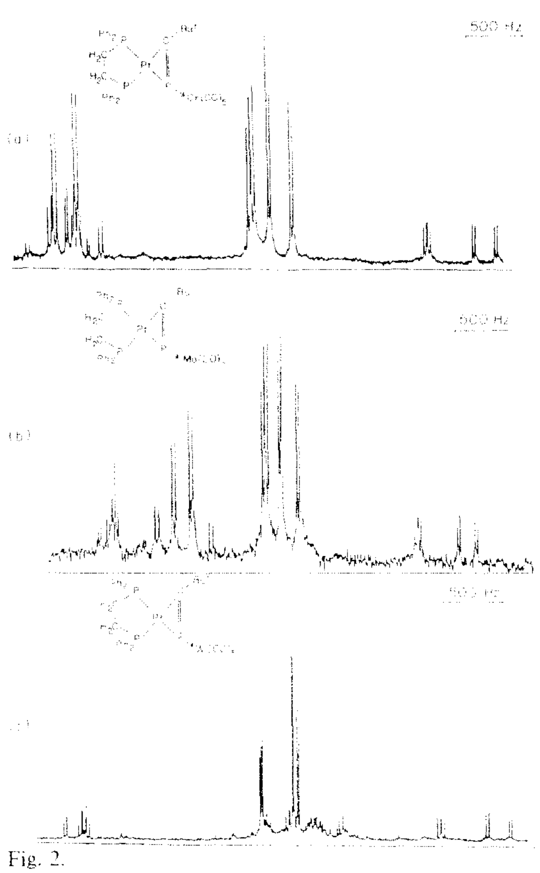


Fig. 2.

2.1. ^{31}P NMR spectra

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

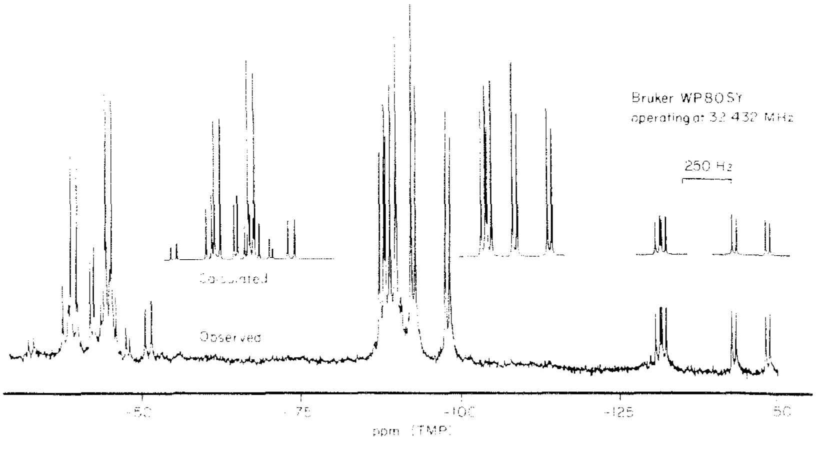
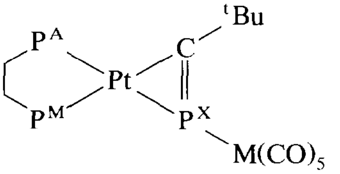


Fig. 3. Observed and calculated $^{31}P\{^1H\}$ NMR spectra for [Pt(dppe)(η^2-^{t}BuC≡P → Cr(CO)$_5$] (2).

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; $^2J_{P(M)P(X)}$ ± 21.0; $^2J_{P(A)P(X)}$ ∓ 28.1 Hz.

Similarly, analysis of the $^{31}P\{^1H\}$ NMR spectrum of [Pt(dppe) (^{t}BuCP)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; $^2J_{P(A)P(M)}$ ± 22.6; $^2J_{P(A)P(X)}$ ± 177.5; $^2J_{P(M)P(X)}$ ∓ 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 ^{t}BuCP *via* the phosphorus lone pair.



M = Cr (**2**)
M = Mo (**3**)
M = W (**4**)
$\widehat{P\quad P}$ = dppe

3. Experimental details

3.1. Preparation of [Pt(dppe) (^{t}BuCP)Cr(CO)$_5$] (2)

A two-fold excess of [Cr(CO)$_5$THF] was prepared in THF solution (100 cm^3) from [Cr(CO)$_6$] (0.127 g, 0.577 mmol). [Pt(dppe) (^{t}BuCP)] (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-dimethylpropylidynephosphine-*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) (^{t}BuCP)] (0.160 g, 0.231 mmol) in THF solution (15 cm^3) was treated with an excess of [Cr(CO)$_4$NBD] (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).

3.2. Preparation of [Pt(dppe) (^{t}BuCP)Mo(CO)$_5$] (3)

Similarly, a two-fold excess of [Mo(CO)$_6$THF] prepared from [Mo(CO)$_6$] (0.152 g, 0.577 mmol) in THF solution (100 cm^3) was treated with [Pt(dppe)(^{t}BuCp)] (0.20 g, 0.288 mmol) to afford the dark red crystalline complex [{1,2-bis(diphenylphosphino)ethane-*P*,*P*}-{2,2-dimethylpropylidynephosphine-*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) (^{t}BuCP)] (0.180 g, 0.259 mmol) and an excess of [Mo(CO)$_4$NBD] (0.10 g, 0.333 mmol) in THF solution (20 cm^3).

3.3. Preparation of [Pt(dppe) (^{t}BuCP)W(CO)$_5$] (4)

In an identical procedure to that described above, a two-fold excess of [W(CO)$_5$THF], prepared from [W(CO)$_6$] (0.263 g, 0.577 mmol) in THF solution (100 cm^3), was treated with [Pt(dppe) (^{t}BuCP)] (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) (^{t}BuCP)] (0.20 g, 0.288 mmol) with an excess of [W(CO)$_4$NBD] (0.150 g, 0.385 mmol) in THF solution (15 cm^3).

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

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