

SYNTHESES OF MIXED TRANSITION METAL CLUSTERS CONTAINING THE COORDINATED PHOSPHAALKYNE ${}^t\text{BuC}\equiv\text{P}$

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(Received May 1st, 1985)

Summary

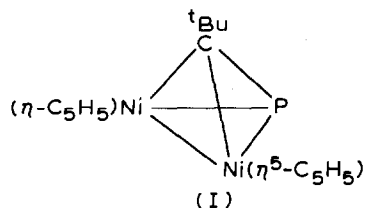
Syntheses of the phosphalkyne complexes $[\text{Ni}_2(\eta^5\text{-C}_5\text{H}_5)_2({}^t\text{BuCP})]$ and $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3({}^t\text{BuCP})]$ are described. Adducts of the latter with $[\text{W}(\text{CO})_5]$ and $[\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ are also reported. The reactions of ${}^t\text{BuCP}$ with $[\text{CoMn}(\text{CO})_9]$ or $[\text{RuCo}_2(\text{CO})_{11}]$ lead to the disproportionation products $[\text{Co}_2(\text{CO})_6({}^t\text{BuCP})]$ and $[\text{Mn}_2(\text{CO})_{10}]$ or $[\text{Ru}_3(\text{CO})_{12}]$, respectively.

Introduction

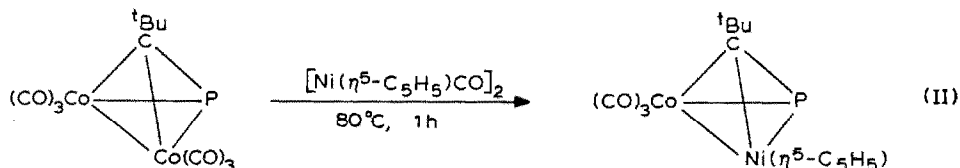
The coordination chemistry of the novel phosphalkyne ligand $\text{RC}\equiv\text{P}$, ($\text{R} = {}^t\text{Bu}$), is rapidly expanding. In previous papers we described the use of ${}^t\text{BuCP}$ to synthesise mononuclear {e.g. $[\text{Pt}(\text{PPh}_3)_2({}^t\text{BuCP})]$ [1], $[\text{Pt}(\text{triphos})({}^t\text{BuCP})]$ [2], dinuclear e.g. $[\text{Co}_2(\text{CO})_6({}^t\text{BuCP})]$ [1], $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4({}^t\text{BuCP})]$ [3] and trinuclear, e.g. $[\text{Fe}_2\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_6({}^t\text{BuCP})]$ [4] complexes as well as compounds in which clusters are interlinked, e.g. $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4({}^t\text{BuCP})\text{M}_3(\text{CO})_{11}]$ ($\text{M} = \text{Ru}, \text{Os}$) [5]. More recently we have synthesised pentametallic complexes of the type $[\text{M}'_3\text{Pd}_2(\text{PPh}_3)_5({}^t\text{BuCP})_3]$, ($\text{M}' = \text{Pd}, \text{Pt}$), [6] which have novel structures. We now describe other synthetic routes to mixed metal complexes containing coordinated ${}^t\text{BuCP}$.

Results and discussion

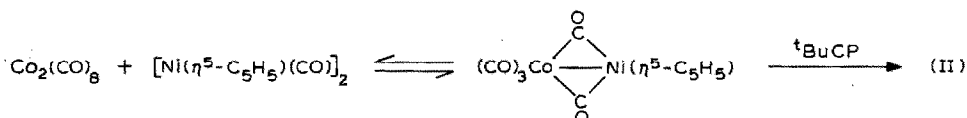
The phosphalkyne ${}^t\text{BuCP}$ reacts readily with $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{CO}]_2$ at room temperature during 3 d to give a high yield of the green crystalline complex $[\text{Ni}_2(\eta^5\text{-C}_5\text{H}_5)_2({}^t\text{BuCP})]$ (I).



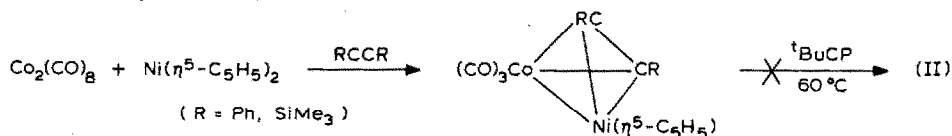
The mixed metal complex $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(^t\text{BuCP})]$ (II) was obtained as a green oil via two different routes. The most efficient method (30% yield) involved heating a mixture of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{CO}]_2$ with the phosphalkyne complex $[\text{Co}_2(\text{CO})_6(^t\text{BuCP})]$ at 80°C in toluene.



Alternatively the mixed metal carbonyl complex $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5]$ [7] was preformed from $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{CO}]_2$ and $[\text{Co}_2(\text{CO})_8]$ and reacted directly with $^t\text{BuCP}$. However the yields of II were much lower (ca. 5%) using this approach.

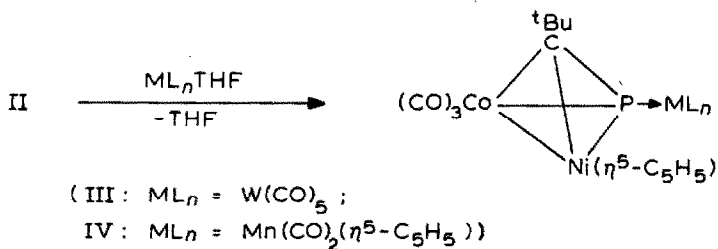


An attempted synthesis of II by treating $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ with $[\text{Co}_2(\text{CO})_6(^t\text{BuCP})]$ was unsuccessful, the only isolated product being $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$. Likewise there was no displacement of alkynes by $^t\text{BuCP}$ from complexes of the type $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{RCCR})]$ ($\text{R} = \text{Ph}, \text{SiMe}_3$) [8].

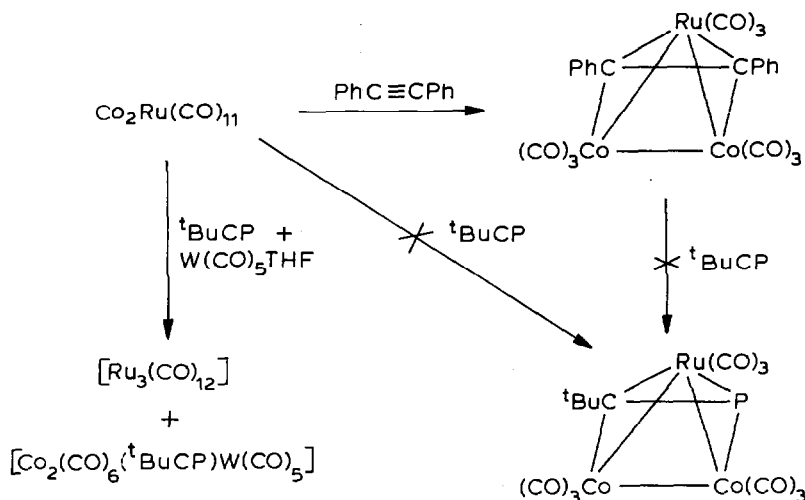


Interestingly, although the ^{31}P (^1H) NMR spectrum of I showed the expected singlet, ($\delta(\text{P}) -47$ ppm (rel. H_3PO_4)), no similar resonance was observable for II presumably because of quadrupole broadening by the ^{59}Co nucleus in this highly asymmetric complex.

The mixed metal complex II readily enters into further coordination to other metal fragments via the phosphorus lone pair. Thus treatment of I with $[\text{WCO}_5(\text{THF})]$ gave a very high yield of the olive green crystalline complex $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(^t\text{BuCP})\text{W}(\text{CO})_5]$ (III)*. The purple oily complex $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(^t\text{BuCP})\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ (IV) was also obtained by displacement of THF from $(\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{THF}))$. As expected IV exhibits two distinct $(\eta^5\text{-C}_5\text{H}_5)$ resonances in the ^1H NMR spectrum, that of the ring attached to Mn occurring as a doublet ($^2J(\text{PCH}) 3.5$ Hz).

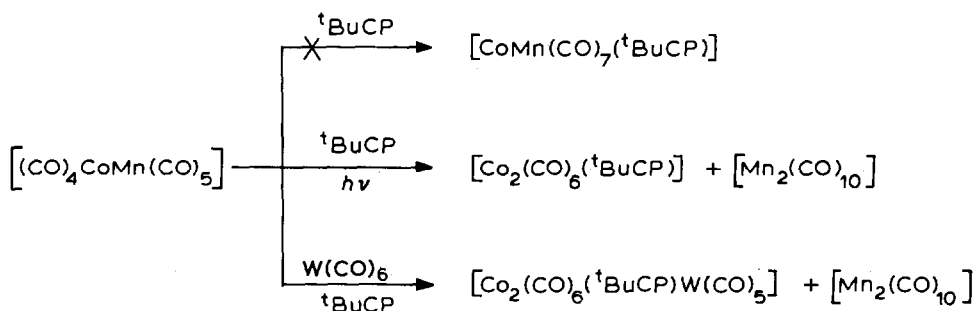


* A single crystal X-ray study on this complex has been carried out [15].



SCHEME 1

In view of the recent report that $[\text{CoMn(CO)}_9]$ [9] reacts with $\text{PhC}\equiv\text{CPh}$ to afford the mixed metal alkyne complex $[\text{CoMn(CO)}_7(\text{PhCCPh})]$ [10] a similar reaction with the phosphalkyne tBuCP was undertaken. No reaction occurred at room temperature, but a sealed tube reaction at 60°C in toluene gave the disproportionation reaction products $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Co}_2(\text{CO})_6(\text{tBuCP})]$. Likewise when a mixture of $[\text{CoMn(CO)}_9]$, $[\text{W(CO)}_6]$ and tBuCP in THF was irradiated with UV light for 16 h at room temperature the products were $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Co}_2(\text{CO})_6(\text{tBuCP})\text{W(CO)}_5]$, e.g.:



Similar observations were made using the recently described $[\text{Co}_2\text{Ru(CO)}_{11}]$ complex reported by Vahrenkamp [11.] Although this compound readily affords the alkyne complex $[\text{Co}_2\text{Ru(CO)}_9(\text{PhCCPh})]$ on treatment with $\text{PhC}\equiv\text{CPh}$ [12,13], no analogous tBuCP product could be obtained either via direct reaction or by alkyne displacement by the phosphalkyne. A mixture of $[\text{Co}_2\text{Ru(CO)}_{11}]$, $[\text{W(CO)}_5(\text{THF})]$ and tBuCP underwent disproportionation to $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Co}_2(\text{CO})_6(\text{tBuCP})\text{W(CO)}_5]$ (see Scheme 1).

These ready disproportionation reactions described above contrast with the easier formation of mixed bimetallic phosphalkyne complexes of the type $[\text{MoW}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\text{tBuCP})]$ to be described elsewhere which have been made by phos-

phaalkyne addition across the metal–metal triple bond of $[\text{MoW}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ [14].

Experimental

Preparation of $[\text{Ni}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{BuCP})]$ (I)

A solution of BuCP (0.1001 g, 1 mmol) in toluene (10 ml) was added to a solution of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$, (0.3036 g, 1 mmol), in toluene (10 ml). The mixture was stirred at room temperature for 3 d then filtered, and the filtrate was concentrated and chromatographed (silica gel, toluene eluent) to give an oil, which gave a green solid on treatment with hexane. (Yield 0.278 g, 80%). Found: C, 51.8; H, 5.50; $\text{C}_{15}\text{H}_{19}\text{Ni}_2\text{P}$ calcd.: C, 51.7; H, 5.71%. ^{31}P : $\delta(\text{P}) - 47$ ppm (rel. H_3PO_4), ^1H : $\delta(\text{H})$ 1.40 (s, Bu) $\delta(\text{H})$ 5.15 (s, C_5H_5).

Preparation of $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{BuCP})]$ (II)

Method a. A solution of $[\text{Co}_2(\text{CO})_6(\text{BuCP})]$, (0.176 g, 0.455 mol), and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$, (0.128 g, 0.455 mmol), in toluene was kept at 80°C for 1 h, during which CO was evolved. After removal of the solvent the product was dissolved in hexane (10 ml), and the solution was filtered then chromatographed on silica gel (hexane eluent) to give the green oily product as the first fraction (0.040 g, 22%) (IR (hexane) 2080vw, 2072vw, 2056m, 2040vs, 2028w, 2016w, 2006s cm^{-1} (carbonyl region), ^1H NMR: $\delta(\text{H})$ 1.2 (v br Bu), $\delta(\text{H})$ 5.2 (v br) (C_5H_5).

Method b. A solution of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (0.152 g, 0.5 mmol) and $[\text{Co}_2(\text{CO})_8]$ (6.171 g, 0.5 mmol) in 20 ml toluene was stirred overnight at room temperature. A solution of 0.100 g (0.1 mmol) BuCP in 10 ml toluene was added and the mixture was stirred for 16 h. The solvent was removed in vacuo and the residue taken up in 10 ml hexane and isolated by chromatography as described in method (a). Yield: 18.3 mg (5%).

Preparation of $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{BuCP})\text{W}(\text{CO})_5]$ (III)

A solution of $[\text{W}(\text{CO})_6]$ (0.405 g, 0.115 mmol) in THF was irradiated overnight with UV light then added to a solution of II, (0.040 g, 0.115 mmol), in THF (5 ml). The mixture was stirred for 3 h at room temperature and after removal of solvent the residue was dissolved in hexane (10 ml). The solution was filtered and the solvent evaporated to give an olive green solid (0.0693 g, 85%). Found: C, 32.9; H, 2.55. $\text{C}_{18}\text{H}_{14}\text{NiO}_8\text{PW}$ calcd.: C, 31.3; H, 2.04% IR (hexane): 2079s, 2056s, 2020s, 20166sh, 1945vs, cm^{-1} (carbonyl region). ^1H NMR $\delta(\text{H})$ 1.2 (br, Bu) $\delta(\text{H})$ 5.2 (br, C_5H_5).

Preparation of $[\text{CoNi}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{BuCP})\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ (IV)

A solution of $[\text{W}(\text{CO})_6]$, (0.405 g, 0.115 mmol), in THF was irradiated overnight with UV light then added to a solution of II (0.040 g, 0.115 mmol) in THF (5 ml). The mixture was stirred for 3 h at room temperature then the solvent was removed and the residue was dissolved in hexane (10 ml). Chromatography on silica gel (hexane eluent) gave a purple fraction, which yielded IV as a purple oil (0.0187 g, 30%) IR (hexane): 2034s, 2000s, 1953s, 1906s cm^{-1} (carbonyl region). ^1H NMR $\delta(\text{H})$ 1.38 (s, Bu) $\delta(\text{H})$ 4.67 (d, $\text{C}_5\text{H}_5(\text{Mn})$, $J(\text{PCH})$ 3.5 Hz) $\delta(\text{H})$ 5.34 (s, C_5H_5).

Reaction of $[\text{CoMn}(\text{CO})_9]$ with BuCP

A mixture of $[\text{CoMn}(\text{CO})_9]$ (0.260 g, 0.710 mmol) (made from $[\text{Co}(\text{CO})_4]\text{Na}$ and

[Mn(CO)₅Br] [9] and ¹BuCP, (0.071 g, 0.710 mmol) in toluene was sealed in a glass tube and kept at 60°C for 16 h. After removal of solvent the residue was dissolved in hexane (10 ml), and chromatography on silica gel (hexane eluent) gave a red oil identified as [Co₂(CO)₆(¹BuCP)] by its characteristic IR spectrum in the carbonyl region. A second product was similarly identified as [Mn₂(CO)₁₀].

Reaction of [CoMn(CO)₉] with ¹BuCP in the presence of [W(CO)₆]

A mixture of [CoMn(CO)₉] (0.183 g, 0.5 mmol), [W(CO)₆] (0.176 g, 0.5 mol), and ¹BuCP (0.050 g, 0.5 mmol) in THF (20 ml) was irradiated with UV light for 16 h. After removal of solvent the residue was dissolved in hexane, and chromatography gave the known red complex [Co₂(CO)₆(¹BuCP)W(CO)₅] and the yellow [Mn₂(CO)₁₀], both identified by their characteristic IR spectra.

Reaction of [RuCo₂(CO)₁₁] with ¹BuCP in the presence of [W(CO)₆]

A solution of [W(CO)₆] (0.343 g, 0.977 mmol) in THF (20 ml) was irradiated for 4 h with UV light then cooled to -30°C and solid [RuCo₂(CO)₁₁] (0.527 g, 0.977 mmol) and ¹BuCP (0.100 g, 1 mmol) in THF (10 ml) were added with stirring. The mixture was slowly warmed to room temperature, CO evolution occurring at about 0°C. The solution was stirred overnight, the solvent was removed, and the residue was extracted with hexane. Chromatography on silica gel gave the red complex [Co₂(CO)₆(¹BuCP)W(CO)₅] (0.187 g, 27%) followed by the yellow [Ru₃(CO)₁₂] complex.

Reaction of [RuCo₂(CO)₉(Ph₂C₂)] with ¹BuCP

[RuCo₂(CO)₉(Ph₂C₂)] was prepared as described in the literature [11]. A solution of [RuCo₂(CO)₉(Ph₂C₂)] (0.100 g, 0.212 mmol) and ¹BuCP (0.022 g, 0.212 mmol) in toluene (20 ml) was stirred overnight at room temperature. The infrared spectrum in the carbonyl region showed only the bands due to the starting material. The mixture was then warmed up to 60°C in a sealed tube, but no reaction took place.

Acknowledgement

We thank the SERC for financial support for this work and Messrs. Johnson-Matthey for the loan of platinum metal salts.

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