

SYNTHESES OF μ^3 - η^2 PHOSPHAALKYNE; COMPLEXES OF TRINUCLEAR IRON AND RUTHENIUM HYDRIDONONACARBONYL ANIONS
 $[M_3H(CO)_9(Bu^tCP)]^-$ (M = Fe, Ru)

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Summary

Syntheses of the anionic μ^3 - η^2 phosphalkyne complexes $[M_3H(CO)_9(Bu^tCP)]^-$ (M = Fe, Ru) are reported.

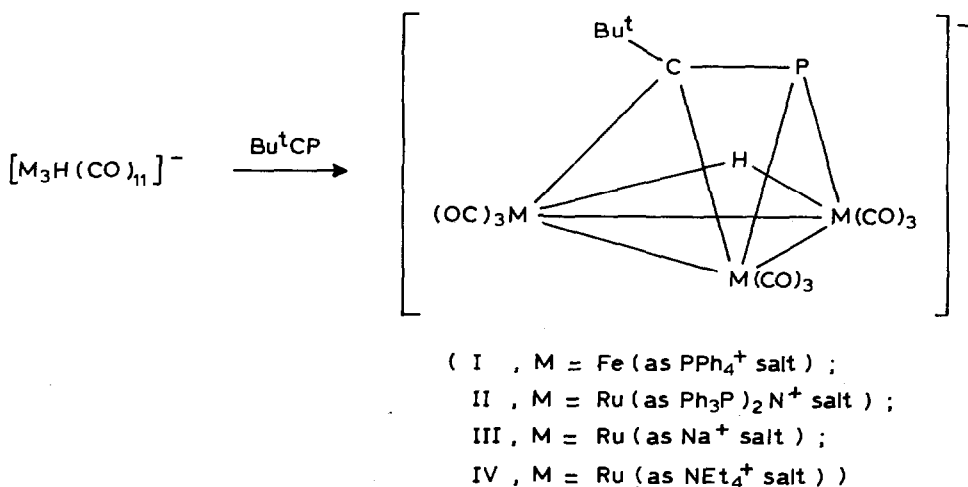
Introduction

Organometallic compounds containing the novel phosphalkyne ligand Bu^tCP are of current interest [1,2] and show similar structural patterns to the better known alkyne and carbyne transition metal compounds. Here we report examples of the first anionic complexes containing coordinated Bu^tCP which have the novel μ^3 - η^2 bonding mode.

Results and discussion

In a recent paper [3] we reported that although $[Co_2Ru(CO)_{11}]$ [4] readily affords the alkyne complex $[Co_2Ru(CO)_9(PhCCPh)]$ on treatment with $PhC\equiv CPh$ [5,6] no analogous phosphalkyne product was formed either by direct reaction or by alkyne displacement with the phosphalkyne $Bu^tC\equiv P$. Likewise a mixture of $[Co_2Ru(CO)_{11}]$, $[W(CO)_5(THF)]$, and Bu^tCP underwent disproportionation to $[Ru_3(CO)_{12}]$ and $[Co_2(CO)_6(Bu^tCP)W(CO)_5]$ [3].

The recent report by Lourdichi and Mathieu [7] that the trinuclear anionic iron complex $[Fe_3H(CO)_{11}]^-$ reacts with Ph_2C_2 to form $[Fe_3H(CO)_{10}(C_2Ph_2)]$, $[Fe_3H(CO)_9(C_2Ph_2)]^-$ and $[Fe_3H(CO)_6(\mu-CO)(C_2Ph_2)]$ prompted us to carry out the related reaction with Bu^tCP , since $[Fe_3H(CO)_{11}]^-$ is isoelectronic with $[Co_2Fe(CO)_{11}]$.



SCHEME 1

Treatment of $[Fe_3H(CO)_{11}][PPh_4]$ with an equimolar amount of Bu^tCP at $0^\circ C$ in either CH_2Cl_2 or tetrahydrofuran readily afforded the brown complex $[Fe_3H(CO)_9(Bu^tCP)]^- [PPh_4]^+$ (I) with evolution of CO (see Scheme 1).

By analogy, treatment of the triruthenium carbonyl anion $[Ru_3H(CO)_{11}]^- [8]$ with Bu^tCP readily gave the phosphalkyne complexes II–IV. All these phosphalkyne complexes I–IV, (which are the first reported anionic systems), were characterised by elemental analysis and IR and NMR spectroscopic properties are listed in Table 1.

The IR spectra of I–IV revealed the presence of only terminal carbonyl ligands and are very similar to that of the related $[Fe_3H(CO)_9Ph_2C_2]^-$ complex, suggesting a similar structure. The proton NMR spectra of complexes I–IV each show the characteristic bridging hydride resonance at high field occurring as a 1/1 doublet arising from coupling to the single phosphorus nucleus of the coordinated Bu^tCP

TABLE 1
 $\nu(CO)$ IR DATA AND 1H AND ^{31}P NMR DATA FOR I–IV

Complex	$\nu(CO)$ ^a	1H ^b	^{31}P ^{a,c}
I	1990m, 1965s, 1945m	δ -21.9 (d, Fe_2H , $J(PH)$ 31 Hz) δ 1.1 (s, 9H, Bu^t) δ 7.4 (s, 20H, Ph)	-118.3 $[PPh_4]^+$ +295.6
II	2020w, 2010sh, 1975m, 1960m, 1940sh	δ -17.4 (d, Ru_2H , $J(PH)$ 19 Hz) δ 1.1 (s, 9H, Bu^t) δ 7.6 (m, 20H, Ph)	-117.4 $[N(PPh_2)_2]^+$ +276.8
III	1980s, 1962m, 1945sh	δ -19.2 (d, Ru_2H , $J(PH)$ 14 Hz) δ 1.1 (s, 9H, Bu^t)	+274.2
(IV)	2010w, 1985s 1965m, 1945sh	δ -17.0 (d, Ru_2H , $J(PH)$ 17 Hz) δ 1.1 (s, 9H, Bu^t) δ 3.48 (q, 12H, CH_3) δ 1.38 (t of t, 8H, CH_2)	+277.5

^a In CH_2Cl_2 . ^b In $CDCl_3$. ^c In ppm (rel. TMP).

ligand (Table 1). Of special interest are the ^{31}P chemical shifts in I–IV, which are all found at significantly higher field than that observed for the free Bu¹CP ligand, presumably reflecting the anionic nature of the phosphaaalkyne complexes.

The common structure exhibited by I–IV presumably involves coordination of the phosphaaalkyne to the trimetallic core in a $\mu^3\text{-}\eta^2$ mode with the phosphorus lone pair presumably playing no bonding role to the trimetallic cluster. This new type of phosphaaalkyne bonding differs from the $\mu^3\text{-}\eta^2 \perp$ mode of bonding we established previously in the complex $[\text{Fe}_2\text{Pt}(\text{dppe})(\text{CO})_6(\text{Bu}^1\text{CP})]$ [9] but is of course directly structurally related to the isoelectronic neutral and anionic alkyne complexes $[\text{MNi}_2(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{C}_2\text{Ph}_2)]$ (M = Fe, Ru) [10] and $[\text{Fe}_2\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_6(\text{C}_2\text{-Ph}_2)]^-$ [11].

Surprisingly in spite of the enhancement basicity of the phosphorus lone pair electrons in I–IV attempts to alkylate the phosphorus in complexes I–IV with MeI, or $[\text{Et}_3\text{O}][\text{BF}_4]$ were unsuccessful, possibly due to electron delocalisation over the metal framework. Likewise we detected no reaction with R_3SnCl (R = Me, Ph). Reactions of $[\text{Fe}_3\text{H}(\text{CO})_{11}(\text{Ph}_2\text{C}_2)]^-$ on the other hand with Et_3O^+ , CPh_3^+ or Ag^+ are known to lead to the formation of the neutral dinuclear complex $[\text{Fe}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)]$ [12]. Very recently we have found that $[\text{Fe}_3\text{H}(\text{CO})_9\text{C}_2\text{Me}_2]^-$ is formed quantitatively from $[\text{Fe}_3(\text{CO})_9\text{C}_2\text{Me}_2]$ by treatment with LiBEt_3H [14].

Experimental

Standard Schlenk techniques and dry distilled solvents were used throughout. ^1H and ^{31}P NMR spectra were recorded with a Bruker WP80 Multinuclear Fourier Transform Spectrometer. Chemical shift data are quoted relative to TMS and TMP, respectively, with upfield shifts negative. Infrared spectra were recorded on a Perkin–Elmer 1430 spectrometer. Elemental analysis were carried out by Mrs A.G. Olney of the School of Chemistry and Molecular Sciences. Bu¹CP was prepared by the method described in ref. 13.

Preparation of $[\text{Fe}_3\text{H}(\text{CO})_9(\text{Bu}^1\text{CP})]^- [\text{PPh}_4]^+$ (I)

A solution of $[\text{Fe}_3\text{H}(\text{CO})_{11}][\text{PPh}_4]$ (0.41 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3) was treated at 0°C with a solution of Bu¹CP (0.05 g, 0.5 mmol) in CH_2Cl_2 (5 cm^3). After 1 h the solution was filtered and the volatiles removed under vacuum. The resulting oily brown complex was washed with hexane (3 × 10 cm^3) using an ultrasonicator and on drying gave dark brown crystals of I (0.38 g, 88%). Found: C, 52.40; H, 4.38. $\text{C}_{38}\text{H}_{30}\text{Fe}_3\text{O}_9\text{P}_2$ calcd.: C, 53.05; H, 3.50%.

Preparation of $[\text{Ru}_3\text{H}(\text{CO})_9(\text{Bu}^1\text{CP})]^- [\text{N}(\text{PPh}_3)_2]^+$ (II)

Similarly a solution of $[\text{Ru}_3\text{H}(\text{CO})_{11}][\text{N}(\text{PPh}_3)_2]$ (0.38 g, 0.33 mmol) in CH_2Cl_2 (10 cm^3) was treated with a solution of Bu¹CP (0.33 mmol) in CH_2Cl_2 (5 cm^3). After 8 h at room temperature the product was isolated in the same way to give the brown crystalline solid II (0.3 g, 77%). Found: C, 50.87; H, 4.00; N, 0.72. $\text{C}_{50}\text{H}_{40}\text{NO}_9\text{P}_3\text{Ru}_3$ calcd.: C, 50.25; H, 3.35; N, 1.17%.

Preparation of $[\text{Ru}_3\text{H}(\text{CO})_9(\text{Bu}^1\text{CP})]^- [\text{Na}]^+$ (III)

Similarly a solution of $[\text{Ru}_3\text{H}(\text{CO})_{11}][\text{Na}]$ (0.31 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3) was treated with Bu¹CP (0.5 mmol) in CH_2Cl_2 (5 cm^3) to yield after 4 days the grey

brown solid III (0.23 g, 67%). Found: C, 23.90; H, 2.08. $C_{14}H_{10}NaO_9PRu_3$ calcd.: C, 24.74; H, 1.47%.

Preparation of $[Ru_3H(CO)_9(Bu^iCP)]^- [NEt_4]^+$ (IV)

In a similar manner a solution of $[Ru_3H(CO)_{11}][NEt_4]$ (0.37 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3) was treated with Bu^iCP (0.5 mmol) in CH_2Cl_2 (10 cm^3). After 8 h the product was isolated as a dark brown crystalline solid IV (0.29 g, 73%). Found: C, 32.84; H, 4.00; N, 1.94. $C_{22}H_{30}NO_9PRu_3$ calcd.: C, 33.57; H, 3.81; N, 1.78%.

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