The unprecedented formation of molybdenum-centred 1,1,4,4-tetrakis(phosphino)buta-1,3-diene from niobium-centred bis(phosphino)acetylene

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Photoreaction between [NbI(CO)$_2$(PMe$_2$Ph)$_2$(Ph$_2$PC≡C-PPh$_2$)] (with the side-on coordinated alkyne acting as a four-electron donor) and [Mo(CO)$_6$] yields the C–C coupling product [{Mo(CO)$_4$}$_2${μ-(Ph$_2$P)$_2$C=CHCH=C-(PPh$_2$)$_2$}], where the ligand coordinates end-on through the four phosphine functions.

In the context of reactivity studies of alkyne–niobium(I) complexes of the general formula [NbX(CO)$_2$(PR$_3$)$_2$(η^2-alkyne)] (X = halogen),[1,2] in which the alkyne donates four electrons, we have observed a new and rather complex reaction for the diphosphabutyne Ph$_2$PC≡CPPh$_2$ [bis(diphenylphosphino)acetylene, dppa], involving transmetallation, rearrangement of P–C bonds, and reductive C–C coupling. The coupling is of interest in connection with reductive C–C coupling reactions between unsaturated organic substrates, catalysed by the systems MCl$_n$–Zn–H$^+$ or MCl$_n$–LiAlH$_4$ (M = V, Nb, Ta),[1b,3,4] which probably contain the metal in a low oxidation state, where it is capable of coordinating and thus activating the substrate.

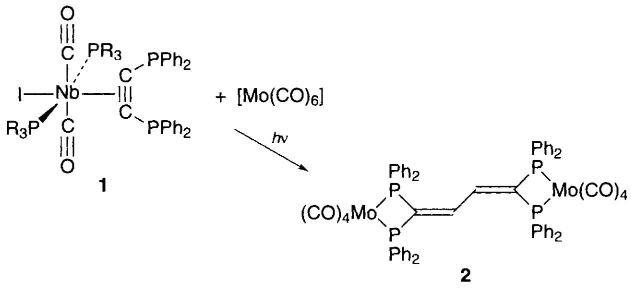
Various reactivity patterns have been reported for dppa. The more common reaction, which leaves the ligand intact, is the end-on terminal and end-on bridging coordination through the phosphorus functions to carbonyl–vanadium,[5] –molybdenum,[6] –manganese,[7] –rhenium,[8] –cobalt,[9] –osmium and –ruthenium,[10,11] or exclusive side-on coordination as in [NbI(CO)$_2$(PMe$_2$Ph)$_2$(η^2-dppa)].[2] In addition, as has been shown for carbonyl–ruthenium, –osmium and –rhenium cluster compounds, {M}, one or two of the PPh$_2$ groups may be cleaved off under thermally or photoinduced conditions to yield ligand fragments such as Ph$_2$P along with C$_2$PPh$_2$,[11a,12] PhC$_2$PPh$_2$[12b] or C$_2$.[8] These fragments, trapped in the clusters as ligands, may take part in coupling reactions in the presence of suitable unsaturated molecules. An example is the C–C coupling between {Ru}C$_2$PPh$_2$ and H$_2$C=CHR to form {Ru}CHRCHCHPPh$_2$.[13] A related coupling reaction is the formation of an iron cluster containing μ_3-η^4-Ph$_2$PC=C(O)Ph from {Fe}CO and Ph$_2$PC≡CPh.[14] A coupling reaction leading to a but-2-ene fragment coordinating *via* P and C has been reported for a chloro–tantalum complex (*vide infra*).[15] Alternately to the cleavage of the Ph$_2$P–C bond, formation of such bonds has also been reported. Thus, the reaction between molybdenum-bound μ-η^2-alkynes HC≡CR and Ph$_2$PCl results in the formation of μ-η^3-(HRC=CPPh$_2$).[6]

[NbI(CO)$_2$(PMe$_2$Ph)$_2$(η^2-dppa)][2] **1** was prepared from [NbI(CO)$_3$(PMe$_2$Ph)$_3$][1b,16] and dppa. In order to evaluate the availability of the phosphorus functions of dppa in **1** for coordination to electron-deficient metal centres, we reacted **1** with [W(CO)$_6$] and [Mo(CO)$_6$], respectively, in thf, which yield {M(CO)$_5$} when irradiated with UV light.

Under these conditions, **1** degrades and the complexes [M(CO)$_3$(PMe$_2$Ph)$_3$] may form as one of the major products (for M = W see ref. 2). In the case of M = Mo, a by-product of composition [{Mo(CO)$_4$}$_2${μ-(Ph$_2$P)$_2$C=CHCH=C-(PPh$_2$)$_2$}] **2** has been identified (Scheme 1),† which yielded crystals suitable for an X-ray structure analysis.‡

Cluster **2** consists of two {Mo(CO)$_4$(PPh$_2$)$_2$} units linked by a buta-1,3-diene backbone (Fig. 1). There is a centre of inversion between the two central CH groups [C(11), C(11a)]. The CC bond lengths in the backbone, 1.358(6) Å for the double bonds, 1.455(9) Å for the single bond, are about normal for this conjugated system which apparently does not incorporate the orbitals localized on the phosphorus functions and involved in metal coordination. The two PPh$_2$ groups, two of the CO groups [CO(3), CO(4)] and Mo form a practically ideal plane, which is coplanar with the butadiene fragment. The two remaining CO groups [CO(1), CO(2)] are in axial positions; the OC–Mo–CO bond angle [172.1(2)°] slightly but significantly deviates from linearity, with the carbonyls bent away from the butadiene unit. The reaction leading to **2** is related to the reaction between [Ta$_2$Cl$_6$(SMe$_2$)$_3$] and dppa in that two C$_2$ fragments couple to form a C$_4$ unit.[15] It differs from the latter reaction in that there is concomitant PPh$_2$ migration.

The mode of formation of **2** is not clear. In the light of the P–C cleavage reactions mentioned above, the initiating step should be the photoinduced homolytic rupture of one of the Ph$_2$P–C bonds in dppa, possibly in an intermediately formed Nb(μ-η^3-dppa)Mo(CO)$_5$ adduct, followed by the generation of a niobium σ-alkenyl complex containing the (CO)$_n$Nb–CH=C(PPh$_2$)$_2$



Scheme 1

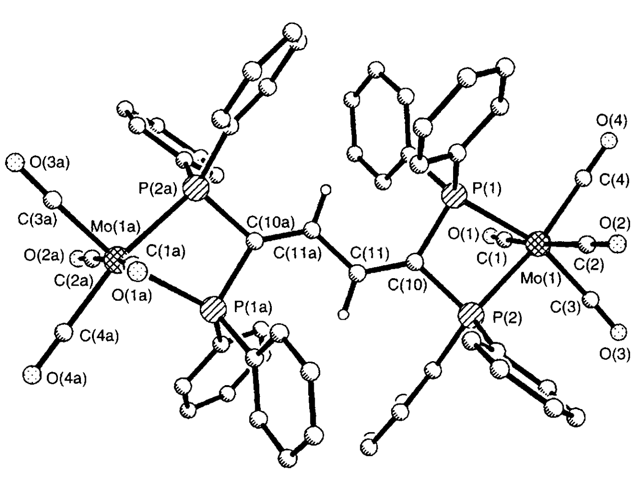


Fig. 1 XP drawing of [{Mo(CO)$_4$}$_2$(μ-dppa)$_2$], **1**

moiety. σ-Alkenyl complexes of composition $[(CO)_{6-n}(\text{phosphine})_nM(\sigma\text{-alkenyl})]$ [M = V,[17] Nb (unpublished work)] have in fact been shown to form in the light-induced reaction between hydrido–vanadium or –niobium complexes and alkynes. The reduction equivalents apparently stem from the Nb^{I} centre of **1**. The intermediate formation of a M–C bond is also plausible in the light of the coupling reaction in the Ta system mentioned above, where a $Ta–C_{\sigma}$ bond forms with simultaneous oxidation of Ta^{III} to Ta^{V}. Preliminary investigations into reactions between $[Mo(CO)_6]$ and complex **1**, modified with respect to the halide (Br instead of I) and the phosphine ($2PMe_3$, $2PEt_3$, $Me_2PCH_2CH_2PMe_2$ instead of $2PMe_2Ph$), confirm that the reaction displayed in Scheme 1 can be generalized to a certain extent.

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Footnotes

† *Preparation of* **2**. All operations were carried out in an inert gas atmosphere and in absolute solvents. 0.394 g (2 mmol) of **1**[2] dissolved in 20 ml of thf was treated with 1.056 g (4 mmol) of $[Mo(CO)_6]$. This reaction mixture, contained in a Duran–Schlenck tube, was cooled to *ca.* −60 °C and irradiated for 6 h with UV light by means of a Philips HPK 125 W high-pressure mercury lamp in a quartz immersion well, placed in the immediate proximity of the reaction vessel. The originally green–brown solution turned dark brown. The solution was filtered, concentrated to the point where precipitation just started, and treated with hexane (one fifth of the solution volume). After standing for 1 week at −25 °C, the majority of unreacted $Mo(CO)_6$ had precipitated. The supernatant brown solution was decanted, and hexane was added so as to provide a thf–hexane ratio of 2 : 1. A brown sticky product of complex composition precipitated. A small amount of the solution was taken apart, and red crystals of **2**·2thf suitable for an X-ray structure analysis separated within months on standing at room temperature. The remainder of the solution was treated with additional hexane (thf–hexane, 1 : 1) leading to the precipitation of a red–brown powder, which was filtered off and dried by passing N_2 through the filter plate to yield 208 mg (16%) of **2**·2thf (Found: C, 60.69; H, 4.51; P, 9.01. $C_{24}H_{29}MoO_5P_2$ requires C, 60.46; H, 4.33; P, 9.17%). ^{31}P NMR(thf–$[^2H_8]$thf, 2 : 1), δ_P 37.

‡ *Crystal data for* **2**·thf: $C_{60}H_{42}Mo_2O_8P_4\cdot 2C_4H_8O$, M = 1350.90, triclinic, space group $P\bar{1}$, a = 10.264(2), b = 11.375(3), c = 14.229(7) Å, α = 104.35(3), β = 93.81(2), γ = 94.98(2)°, Z = 1, U = 1596.7(9) Å^3, D_c = 1.405 g cm^{-3}, $F(000)$ = 690, μ(Mo-Kα) = 5.5 cm^{-1}. Final $R1$ = 0.0482 $[wR2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{\frac{1}{2}}]$ = 0.1014 for 4136 reflections with $I > 2\sigma(I_o)$ measured in the range $2.38 < \theta < 25.06°$ at 173 K on a Hilger & Watts diffractometer. Residual electron density: max. 0.874, min. −0.871 e Å^{-3}; 392 parameters were refined. The refinement was carried out with the SHELXL-93 program. The carbon atom C^3 [= C(40)] of the thf of crystallization was treated with a 1 : 1 disorder model. The disorder corresponds to a conformational change of the five-ring (flipping up and down of C^3). Hydrogen atoms were placed in calculated ideal positions and refined with isotropic temperature factors. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/109.

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