A σ-Phosphaalkyne Complex of Ruthenium(0)

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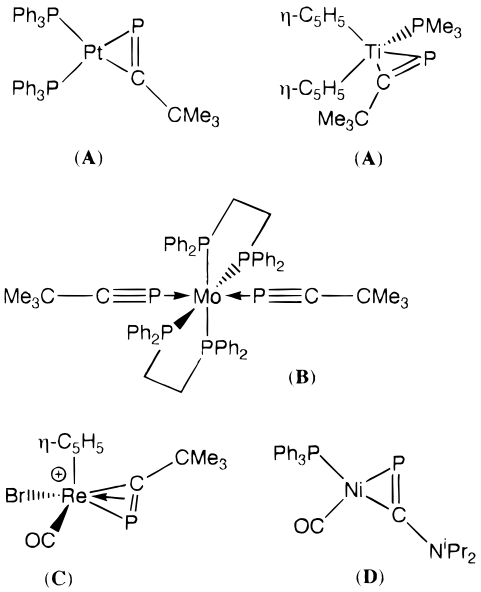
Introduction

More than a decade after Nixon's synthesis of the archetypal phosphaalkyne complex $[Pt(\eta^2\text{-}P{\equiv}C^tBu)(PPh_3)_2]$[3] the range of simple mononuclear coordination complexes of the ubiquitous phosphaalkyne $P{\equiv}C^tBu$ remains surprisingly small despite enormous effort expended in the field.[4] Exemplary coordination types are shown in Chart 1, which highlights features to have emerged in the interim, i.e., (**A**) dihapto coordination (π-P,C),[5] (**B**) monodentate coordination (σ-P),[6] (**C**) four-electron coordination,[7] and (**D**) the use of the reversed polarity phosphaalkyne $P{\equiv}CN^iPr_2$.[8] The scarcity of simple π-adduct complexes should not be taken to in any way weaken the extremely useful and extensively demonstrated analogy with alkynes. Rather, the situation has arisen because of the unparalleled facility of phosphaalkynes to enter into metal-mediated oligomerizations and the propensity of both the monomer and derived oligomers to support polymetallic ensembles. Furthermore, coordination of a phosphaalkyne to metal centers is often followed by coupling reactions with ligands for which nonspectatorial roles are common. Such ligands have so far included alkylidynes,[9] vinylidenes,[10] carbenes,[11] arynes,[12] alkoxides,[11c] and very recently the simplest of all ligands, the hydride.[13] Finally, while coordination to a metal center typically stabilizes the P≡C multiple bond, it does not always deactivate it sufficiently to protect it from reactions with adventitous moisture or even complex counteranions, *e.g.*, BF_4 and PF_6.[6b,13b,14]

Chart 1. Mononuclear Phosphaalkyne Complexes



Herein we report the preparation and isolation of the first phosphaalkyne complex of ruthenium wherein the rare monohapto (σ-P) mode of coordination is adopted. The complex is based on the "super mesityl" phosphaalkyne P≡CR′ (hereafter $R' = C_6H_2{}^tBu_3$-2,4,6),[15] the coordination chemistry of which has otherwise not been reported.

Results and Discussion

The complexes $[M(CO)_2(PPh_3)_3]$ (M = Ru, Os)[16] react with internal alkynes[17] and diynes[18] to form π-alkyne complexes of formally zerovalent ruthenium (Scheme 1). Subsequent alkyne oligomerization processes have not been observed to date. The reaction of $[Ru(CO)_2(PPh_3)_3]$ (**1**) with $P{\equiv}C^tBu$ in benzene-d_6 at room temperature was therefore investigated by phosphorus-31 NMR spectroscopy. The singlet peak at δ 49.7 ppm due to **1** was replaced by resonances due to a multitude of compounds that arose. The mixture of compounds proved inseparable in our hands, and none predominated sufficiently for structural assignments to be made with any confidence based on spectroscopic data (IR, NMR) for the mixture.

Although the coordination chemistry of P≡CR′ has yet to be investigated, it seemed reasonable that steric encumbrance at the carbon of the phosphaalkyne might help to prevent any oligomerization processes. This proved to be the case: Treating

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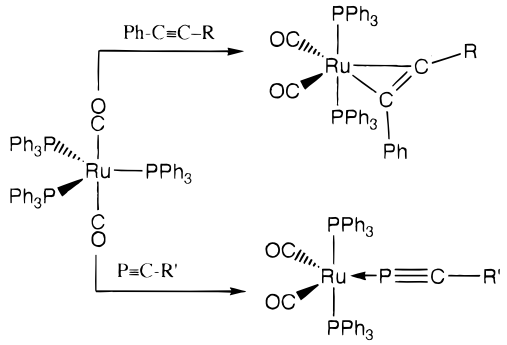
Scheme 1. Reactions of $[Ru(CO)_2(PPh_3)_3]$ with Alkynes and Phosphaalkynes (R = Ph, C≡CPh; R′ = $C_6H_2{}^tBu_3$-2,4,6)



1 with an excess of P≡CR′ in benzene-d_6 or CD_2Cl_2 led to complete disappearance of **1** within 3 h. During this time, the singlet $^{31}P\{^1H\}$ NMR resonance due to **1** was replaced by a singlet at δ −5.4 ppm (liberated PPh_3), a triplet at δ 45.3 ppm, and a doublet at δ 50.5 ppm, the latter two showing mutual coupling of 42.2 Hz. Notably, when this solution was allowed to stand for 24 h, the resonance due to liberated phosphine had decreased substantially, relative to those of the AB_2 system and this decrease was accompanied by the emergence of a myriad of peaks due to at least five new and as yet unidentified compounds. If however the initial product was isolated immediately, free of phosphine, samples redissolved in CH_2Cl_2 appeared more stable. From this we infer that the 1 equiv of phosphine liberated in the reaction plays a rôle in the subsequent decomposition of the product.

Crystallographic grade crystals have yet to be obtained, and so the formulation of the complex rests on FAB-MS and spectroscopic data: The FAB-mass spectrum, while devoid of a molecular ion, shows significant isotopic envelopes attributable to the free phosphaalkyne and the complex fragments $[RuH(CO)_2(PPh_3)_2]^+$, $[RuH(CO)(PPh_3)_2]^+$, and $[Ru(PPh_3)_n]^+$ (n = 1, 2). The ^1H NMR spectrum confirms, by integration, the PPh_3/PCR′ ratio of 2:1. The ^{t}Bu groups give rise to two singlet resonances in the ratio 1:2 indicating that, at least within the ^1H NMR time scale, the two *ortho* positions of the R′ group are chemically equivalent. The infrared spectrum shows two intense carbonyl associated absorptions at 1941 and 1888 cm^{-1}, and on the basis of relative intensities,[19] the two cis-disposed carbonyls would appear to subtend an angle of approximately 110°. While the free phosphaalkyne P≡CR′ has two strong absorptions at 1597 and 1529 cm^{-1}, attributable to the P≡C stretch, no such absorption could be identified in the complex, suggesting perhaps a reduction in the polarity of this bond upon coordination. The AB_2 spin system evident in the ^{31}P NMR spectrum indicates that the phosphines are chemically equivalent. This in combination with the preceding data and the virtual triplet patterns for the ^{13}C NMR resonances due to the phosphine aryl groups indicate coordination of the phosphaalkyne to a C_{2v} $Ru(CO)_2P_2$ fragment with axial phosphines and equatorial carbonyl ligands. Consistent with this the carbonyl resonance appears as a double triplet.

Two isomeric structures may be considered depending on the mode of coordination of the phosphaalkyne, *viz. monohapto* through P (**B**) or *dihapto* through P and C (**A**). The third isomer, with cis-equatorial phosphines and trans-axial carbonyls is inconsistent with IR and ^{13}C and ^{31}P NMR data. We are inclined to favor the less common, *monohapto* coordination mode (**B**) for the the following reasons. (i) The chemical equivalence of the *ortho* substituents of the R′ group is consistent with either the linear Ru−P−C linkage of **B** or rapid rotation of the R′ group around the C−R′ bond of isomer **A**. This latter interpretation seems extremely unlikely given the enormous steric profile of the R′ group. (ii) The magnitude of the ^2J(PP) coupling constant (42.2 Hz) is anomalously large for a *cis*-P−M−P arrangement for π-bound phosphaalkyne complexes (e.g., 24 Hz for $[Pt(\eta^2\text{-}P{\equiv}C{}^tBu)(PPh_3)_2]$[3]) but more in line with those found (37.8−40.3 Hz) for the complexes $[Mo(\sigma\text{-}PC{}^tBu)_2(R_2\text{-}PCH_2CH_2PR_2)_2]$ (R = Et, Ph, C_6H_4Cl, C_6H_4Me).[6a] Furthermore, the thioxophosphane and selenoxophosphane complexes $[Os(\pi\text{-}L)(CO)_2(PPh_3)_2]$ (L = HPS, HPSe, MePS) reported by Roper[20] which are notionally related to **A** show ^2J(PP) couplings in the range 5.1−16.6 Hz. This dramatic increase in the ^2J(PP) value for the present complex is consistent with the increased s character of the hybridization at the phosphaalkyne phosphorus for **B** (sp) relative to **A** (sp^2). Furthermore, the value for ^1J(P≡C) increases upon coordination from 54 Hz in PCR′ to 95 Hz in the complex, when a reduction might have been expected for **A**. (iii) Infrared data associated with the *cis*-$Ru(CO)_2$ unit has been used as an indication of the acceptor ability of ligands "L" in the complexes $[Ru(L)(CO)_2(PPh_3)_2]$.[21] The Cotton−Kraihanzel force constant calculated for the present compound (14.80 N m^{-1}) lies at the low end of the range observed to date for such complexes. This value is comparable to that found for tolane (14.93 N m^{-1}) but considerably lower than those found for other π-bound C-element multiple bonds, e.g., CS_2 (15.80) and CSe_2 (15.92 N m^{-1}). These data therefore suggest that the phosphaalkyne is assuming a primarily σ-dative rather than π-acidic role. These considerations lead us, in the absence of structural data, to formulate the complex as a rare example of a σ-bound phosphaalkyne complex, a situation which is favored by the extraordinary steric profile of the "super mesityl" substituent. It should be pointed out that the only other examples[6a] of such a coordination mode also involve a situation where steric forces would be expected to strongly disfavor the more common π-P,C coordination.

Experimental Section

The compounds $[Ru(CO)_2(PPh_3)_3]$[16] and P≡CR′[15] have been described previously. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube and vacuum line techniques. Solvents were purified by distillation from an appropriate drying agent and degassed prior to use.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 400 NMR spectrometer and calibrated against internal C_6D_6 (^1H) or external H_3PO_4 (^{31}P). Infrared spectra were recorded from Nujol mulls using a Perkin-Elmer 1725-X FT-IR spectrometer. FAB mass spectrometry was carried out using a VG-Autospec instrument using 3-nitrobenzyl alcohol as matrix.

Preparation of $[Ru(P{\equiv}CR')(CO)_2(PPh_3)_2]$. A solution of $[Ru(CO)_2(PPh_3)_3]$ (165 mg, 0.18 mmol) in dichloromethane (8.0 mL) was treated with a solution of P≡CR′ (61 mg, 0.21 mmol) in dichloromethane (1.0 mL). The orange-yellow solution was stirred for 3.5 h, during which time the mixture darkened in color. After ensuring that the reaction had proceeded to completion (^{31}P NMR), the solvent was removed under reduced pressure. The residue was washed thoroughly with hexane to remove excess P≡CR′ and liberated phosphine. The pale yellow product was then dried in vacuo. Yield: 50 mg (30%). Mp: 151−154 °C (dec). The compound could be recrystallized from a mixture of benzene and hexane but decomposed slowly in chlorinated solvents.

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IR (Nujol): 1941 s, 1888 vs [ν(CO)], 1305 w cm^{-1}. NMR (C_6D_6, 25 °C): ^{1}H, δ 1.34 [s, 9 H, CMe_3-4], 1.72 [s, 18 H, CMe_3-2,6], 6.60−8.00 [m × 7, 33 H, C_6H_5 and C_6H_2] ppm; ^{13}C{^{1}H}, 210.3 [CO, dt, $J(P_2C) \approx J(PC) = 16.6$ Hz], 158.7 [P≡*C*, d, $J(PC) = 95$ Hz], 153.8 [d, $C^{2,6}(C_6H_2)$, $J(PC) = 11$ Hz], 147.7 [d, $C^1(C_6H_2)$, $J(PC) = 6$ Hz], 134.5 [vt, $C^1(C_6H_5)$, $J(P_2C) = 23.4$ Hz], 134.0 [vt, $C^{2,6}(C_6H_5)$, $J(P_2C) = 6$ Hz], 129.8 [s, $C^4(C_6H_5)$], 128.1 [vt, $C^{3,5}(C_6H_5)$, $J(P_2C) = 4.5$ Hz], 120.6 [s, $C^{3,5}(C_6H_2)$], 37.1, 34.9 [s × 2, *C*Me_3], 31.1, 30.9 [s × 2, CH_3]; ^{31}P{^{1}H}, δ 45.3 [t, 1 P, $J(PP) = 42.2$ Hz], 50.5 [d, 2 P, $J(PP) = 42.2$ Hz] ppm. FAB-MS (nba) {*m*/*z* (abundance) [assignment]}: 682 (21) [$HRu(CO)_2(PPh_3)_2^+$], 654 (72) [$HRu(CO)(PPh_3)_2^+$], 625 (36) [$HRu(PPh_3)_2^+$], 288 (50) [PCR′$^+$], 363 (100) [$RuPPh_3^+$], 263 (63) [$HPPh_3^+$]. Satisfactory elemental data: not obtained due to solution instability.

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