DOI: 10.1002/ejic.200701330

Synthesis, Characterization and Reactivity of a η^1-Methylphosphaalkyne Complex, $[RuH(dppe)_2(\eta^1\text{-}P{\equiv}CMe)][CF_3SO_3]$

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Keywords: Phosphaalkynes / Main-group elements / Low coordination / Coordination complex

The synthesis of the first example of a complex in which methylphosphaalkyne solely η^1-coordinates a metal center, $[RuH(dppe)_2(\eta^1\text{-}P{\equiv}CMe)][CF_3SO_3]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane], is reported. Treatment of this compound with HBF_4 (acting as a source of HF) has led to the reduction of the phosphaalkyne and the formation of a rare PF_2Et complex, $[RuH(dppe)_2(\eta^1\text{-}PF_2Et)][BF_4]$. Both complexes have been crystallographically characterized.

Introduction

The coordination chemistry of sterically stabilized phosphaalkynes, e.g. P≡C*t*Bu, has been extensively developed over the past two decades.[1] These compounds can ligate mono-, di- and polymetallic fragments in a number of modes involving electron donation from the P-lone pair and/or the P≡C bond of the phosphaalkyne. However, complexes which encompass solely η^1-P-ligating phosphaalkynes are very rare.[2] This results from their P–C bond polarization, $^{\delta+}P{\equiv}C^{\delta-}$, and their relatively high-energy π-orbital HOMOs which lead to them being more alkyne than nitrile like in their coordination chemistry. Generally, η^1-P-coordination of phosphaalkynes to metal fragments only occurs if η^2-P≡C coordination is precluded by the steric properties of the metal fragment. Such a situation occurs in, for example, *trans*-$[W(dppe)_2(\eta^1\text{-}P{\equiv}C\textit{t}Bu)_2]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane],[2f] which was prepared by displacement of the labile dinitrogen ligands from *trans*-$[W(dppe)_2(\eta^1\text{-}N_2)_2]$ upon its treatment with P≡C*t*Bu.

In the past two years we have begun to study the further chemistry of the sterically unhindered phosphaalkyne, P≡CMe, the phosphorus analogue of acetonitrile and propyne. This study has shown that P≡CMe is, in general, significantly more reactive than its hindered counterparts. Its propensity to ligate metal centers in an η^2-fashion has been demonstrated,[3] it has been shown to readily cyclodimerize within the coordination sphere of transition metals,[3] and a number of novel heterocyclic and cage products have resulted from its cycloaddition reactions with a variety of unsaturated substrates.[4,5]

We wished to extend the chemistry of P≡CMe to the formation of complexes in which it acts as a η^1-P ligand. This was seen as of fundamental interest because the properties of such complexes could be compared with those incorporating bulkier phosphaalkynes. In addition, we wished to explore the reactivity of P≡CMe towards nucleophiles and electrophiles within the metal coordination sphere, as very novel results have been achieved with bulkier phosphaalkynes in this respect. The preliminary results of our endeavors in this area are reported herein.

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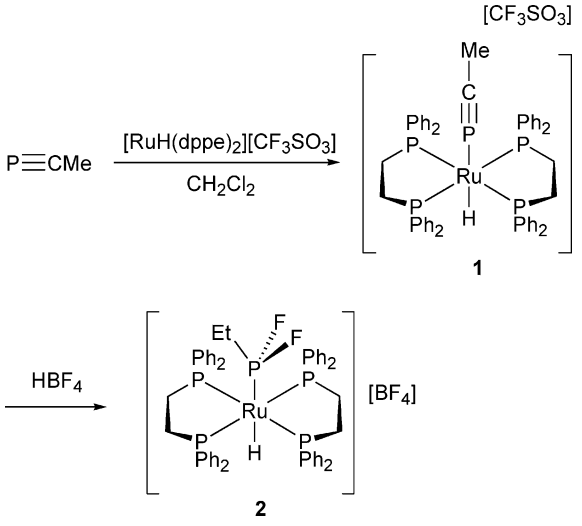
Results and Discussion

As the dinitrogen ligands of *trans*-$[W(dppe)_2(\eta^1\text{-}N_2)_2]$ have been shown to be readily displaced by P≡C*t*Bu, we believed its treatment with the less hindered phosphaalkyne, P≡CMe,[6] would lead to a similar result. Surprisingly, however, no reaction occurred. This is perhaps because the lesser electron donating properties of the methyl group relative to *tert*-butyl lead to P≡CMe being a weaker Lewis base than P≡C*t*Bu. As a result, bulky, coordinatively unsaturated metal fragments were sought which could potentially coordinate P≡CMe without the need for it to displace other ligands. The cationic complexes $[MH(dppe)_2]^+$ (M = Ru[2a] or Fe[7]) were chosen because bulky phosphaalkynes (P≡CR, R = *t*Bu, $SiPh_3$, CPh_3) are known to readily ligate them in an η^1-fashion.

The reaction of $[RuH(dppe)_2][CF_3SO_3]$ with P≡CMe in dichloromethane led to a high yield of the thermally stable target complex, **1**, after recrystallization from a dichloromethane/hexane mixture (Scheme 1). In contrast, the corresponding reaction with $[FeH(dppe)_2][BPh_4]$ was not clean and although the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture suggested the presence of $[FeH(dppe)_2(P{\equiv}CMe)][BPh_4]$, this compound could not be isolated upon work-up and only an intractable mixture of products was obtained. The spectroscopic data for **1** are fully consistent with its proposed formulation. Of most note is its

$^{31}P\{^{1}H\}$ NMR spectrum which displays a doublet signal for the dppe ligands (δ = 61.5 ppm, $^{2}J_{PP}$ = 30 Hz) and a quintet for the phosphaalkyne at a chemical shift (δ –38.7 ppm) significantly downfield from that of the free phosphaalkyne (δ –61.0 ppm).[6] The hydride signal in the ^{1}H NMR spectrum of the compound appears as a doublet of quintets (δ –9.60 ppm, $^{2}J_{PH}$ = 127 and 17 Hz). Similar spectral patterns have been observed for the complexes, $[RuH(dppe)_2(P{\equiv}CR)][CF_3SO_3]$ (R = $SiPh_3$[2b] or CPh_3[2a]).



Scheme 1. Synthesis of complexes **1** and **2**.

The X-ray crystal structure of **1** was determined and its cationic component is depicted in Figure 1. Its P–C triple bond length [1.535(6) Å] is close to those in the few structurally characterized free phosphaalkynes [e.g., 1.538(2) Å in $P{\equiv}CCPh_3$[2a] and 1.532 Å (mean) in the diphosphaalkyne, $P{\equiv}CC(C_6H_4)_3CC{\equiv}P$],[8] but significantly shorter than the P–C bonds in η^2-complexes of methylphosphaalkyne {e.g. 1.617 Å in $[Pt(PCy_3)_2(\eta^2\text{-}P{\equiv}CMe)]^3$}. Although the phosphaalkyne in **1** is close to linear, its coordination to the distorted octahedral ruthenium center deviates significantly from linear [Ru–P–C 153.7(2)°] because of interactions with the surrounding phenyl groups.

It seemed that compound **1** could prove useful as a platform to test the further reactivity of P≡CMe towards electrophiles and nucleophiles. A prior theoretical study on P≡CMe concluded that its methyl protons are quite acidic and that it should be more easily deprotonated than, for example, N≡CMe.[9] Accordingly, we treated **1** with a variety of bases (e.g. NaOH, KO*t*Bu, NaOPh and LiN*i*Pr) but all reactions led to intractable mixtures of products. It is noteworthy that treatment of the related complex, $[RuH(dppe)_2(P{\equiv}CSiPh_3)]^+$, with NaOPh has recently been reported to give the first terminal "cyaphide" complex, $[RuH(dppe)_2(C{\equiv}P)]$.[2b] Attention then turned to the reaction of the electrophilic reagent, MeI, with **1** in CH_2Cl_2. Monitoring this reaction by ^{31}P NMR spectroscopy revealed that a compound was formed at ca. –50 °C with a spectral pattern similar to that of **1**, but with the signal derived from the phosphaalkyne shifted by ca. 200 ppm

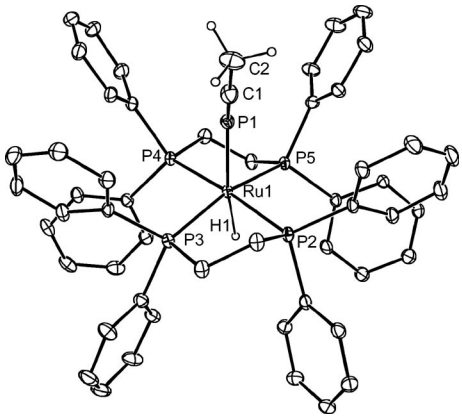


Figure 1. Structure of the cationic component of **1** (25% thermal ellipsoids, dppe hydrogen atoms omitted for sake of clarity). Selected bond lengths [Å] and angles [°]: Ru(1)–P(1) 2.3148(13), Ru(1)–P(5) 2.3453(11), Ru(1)–P(2) 2.3592(11), Ru(1)–P(4) 2.3682(11), Ru(1)–P(3) 2.3786(11), P(1)–C(1) 1.535(6), C(1)–C(2) 1.474(8), C(1)–P(1)–Ru(1) 153.7(2), C(2)–C(1)–P(1) 174.7(5), P(2)–Ru(1)–P(3) 80.82(3), P(5)–Ru(1)–P(4) 82.94(4).

down field (δ = 165.6 ppm, quint., $^{2}J_{PP}$ = 28 Hz, 1 P; δ = 65.2 ppm, d, $^{2}J_{PP}$ = 28 Hz, 4 P). This observation suggests the product contains a P-coordinated phosphaalkene or phosphaalkenyl fragment, though its structure cannot be certain.[10] Upon warming the reaction mixture past –10 °C, the product appeared to decompose to an unidentifiable mixture of phosphorus containing products which prohibited isolation and further characterization of the compound.

Previous studies have shown that bulky η^1-P-coordinated phosphaalkynes can be transformed to, for example, phosphaalkenes,[2c] phosphanes[2c] and phosphorus heterocycles[2a] upon treatment with proton sources. In a similar vain, we examined the reaction of **1** with an excess of a diethyl ether solution of HBF_4 which led to a moderate yield of the difluorophosphane complex, **2** (Scheme 1), after recrystallization from a hexane/dichloromethane solution. In this reaction the HBF_4 is presumably acting as a source of HF which doubly reduces the coordinated phosphaalkyne. The HBF_4 is also the source of the counter anion in **2**. It is noteworthy that P≡C*t*Bu {within the complex *trans*-$[FeH(dppe)_2(\eta^1\text{-}P{\equiv}C\textit{t}Bu)]^+$} has been similarly reduced to $F_2PCH_2\textit{t}Bu$ by treatment with HBF_4.[2c] In that reaction, the stepwise nature of the reduction was confirmed by the isolation of an intermediate containing a P-coordinated fluorophosphaalkene, FP = CH*t*Bu. No similar intermediate (viz. *trans*-$[RuH(dppe)_2\{\eta^1\text{-}P(F){=}C(H)Me\}]^+$) was observed in the current reaction, which is perhaps in line with the previously demonstrated greater reactivity of P≡CMe over P≡C*t*Bu. Indeed, treating **1** with one equivalent of HBF_4 led only to a mixture of **2** and unreacted **1**.

The spectroscopic data for **2** are compatible with its solid-state structure. In its $^{31}P\{^{1}H\}$ NMR spectrum the fluorophosphane signal appears as a triplet of quintets at low field (δ = 244.4 ppm) displaying characteristic $^{1}J_{PF}$ and $^{2}J_{PP}$ couplings (1094 and 30 Hz, respectively). The low field position of this signal is not surprising in light of the electron-

withdrawing nature of the fluorine substituents and it can be compared to a chemical shift of δ = 279.5 ppm for the corresponding signal in the spectrum of *trans*-[FeH(dppe)$_2$-{η¹-P(F)$_2$C(H)$_2$*t*Bu}]$^+$.[2d] The structure of the cationic component of **2** (Figure 2) reveals its ruthenium center to have a similar octahedral geometry to that of **1**, while the geometry of the PF_2Et ligand is unremarkable. Saying this, there has been no previous crystallographic elucidation of this phosphane.

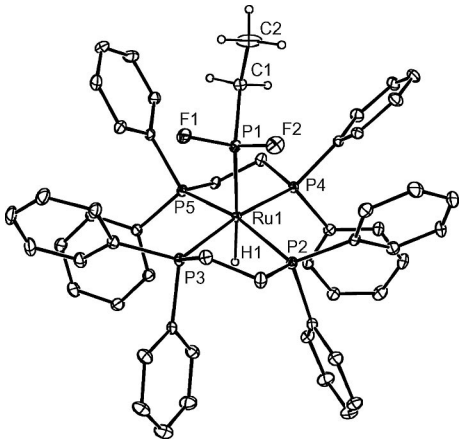


Figure 2. Structure of the cationic component of **2** (25% thermal ellipsoids, dppe hydrogen atoms omitted for sake of clarity). Selected bond lengths [Å] and angles [°]: Ru(1)–P(1) 2.2941(13), Ru(1)–P(5) 2.3394(12), Ru(1)–P(3) 2.3607(13), Ru(1)–P(4) 2.3684(13), Ru(1)–P(2) 2.3783(13), P(1)–F(2) 1.583(3), P(1)–F(1) 1.610(3), P(1)–C(1) 1.811(4), C(1)–C(2) 1.518(7), F(2)–P(1)–F(1) 98.66(15), F(2)–P(1)–C(1) 103.21(19), F(1)–P(1)–C(1) 96.86(18), P(3)–Ru(1)–P(2) 78.79(4), P(5)–Ru(1)–P(4) 84.40(4), C(2)–C(1)–P(1) 115.6(3).

Conclusions

We have reported the synthesis and characterization of the first example of a complex in which methylphosphaalkyne solely η¹-coordinates a metal center. Preliminary reactivity studies have shown that the phosphaalkyne can be reduced to difluoroethylphosphane within the coordination sphere of this complex. This result lays the ground-work for further transformations of this, and other, unhindered, metal-coordinated phosphaalkynes. Work in this area is ongoing in our laboratory.

Experimental Section

Synthesis of [RuH(dppe)$_2$(η¹-P≡CMe)][CF$_3$SO$_3$] (1): P≡CMe (0.56 mL of a 0.34 M solution in diethyl ether, 0.190 mmol) was added to a solution of [RuH(dppe)$_2$][CF$_3$SO$_3$] (100 mg, 0.101 mmol) in dichloromethane (10 mL) at 20 °C to give a yellow solution. After 3 h volatiles were removed in vacuo and the residue dissolved in dichloromethane (1 mL). Layering this with hexane (10 mL) yielded **1** as yellow crystals overnight (yield 90 mg, 75%). M.p. 188–190 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = –9.6 [d of quin, $^2J_{P(dppe)H}$ = 17, $^2J_{P(PCMe)H}$ = 127 Hz, 1 H, Ru*H*], 2.02 (d, $^3J_{PH}$ = 14 Hz, 3 H, CH_3) 2.10 (br., 4 H, CH_2), 2.52 (br., 4 H, CH_2), 7.01–7.32 (m, 40 H, Ar-*H*) ppm. ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6, 298 K): δ = –38.7 (quin, $^2J_{PP'}$ = 30 Hz, *P*CMe), 61.5 (d, $^2J_{PP'}$ = 30 Hz, dppe) ppm. ^{19}F{^{1}H} NMR (281.3 MHz, C_6D_6, 298 K): δ = –78.5 (s, CF_3SO_3) ppm. IR (Nujol): $\tilde{\nu}$ = 1560 [w (P≡C)], 1458 (m), 1376 (m), 1309 (m), 1272 (m), 1187 (m), 1053 (m), 998 (m) cm^{-1}. (MS/EI): *m*/*z* (%) = 958 (3) [RuH(dppe)$_2$(PCMe)$^+$], 899 (32) [RuH(dppe)$_2^+$], 398 (100) [dppe$^+$].

Synthesis of [RuH(dppe)$_2$(η¹-PF$_2$Et)][BF$_4$] (2): HBF_4 (0.18 mL of a 54% solution in Et_2O, 0.135 mmol) was added to a solution of **1** (50 mg, 0.045 mmol) in dichloromethane (5 mL) at 20 °C. After 12 h volatiles were removed in vacuo and the residue dissolved in dichloromethane (1 mL). Layering this with hexane (10 mL) yielded **2** as yellow crystals overnight (yield 20 mg, 40%). M.p. 176–182 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = –7.9 (d of quin, $^2J_{PH}$ = 115 and 21 Hz, 1 H, Ru*H*), 2.06–2.50 (m, 8 H, PCH_2 and 3 H, CH_3), 2.80 (m, 2 H, PCH_2), 7.11–7.33 (m, 40 H, Ar-*H*) ppm. ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 298 K): δ = 62.5 (d, $^2J_{PP'}$ = 30 Hz, dppe), 244.4 (tr. of quin, $^2J_{PP'}$ = 30, $^1J_{PF'}$ = 1094 Hz, *P*F$_2$) ppm. ^{19}F{^{1}H} NMR (281.3 MHz, CD_2Cl_2, 298 K): δ = –153.2 (4 F, B*F*$_4$), –56.2 (d, $^1J_{PF}$ = 1094 Hz, 2 F) ppm. IR $\tilde{\nu}$ (Nujol): $\tilde{\nu}$ = 1376 (m), 1261 (m), 1225 (m), 1029 (m), 890 (m) cm^{-1}. (MS/EI): *m*/*z* (%) = 1000 (83) [RuH(dppe)$_2$(PF$_2$Et)$^+$], 899 (100) [RuH-(dppe)$_2^+$].

Reproducible microanalyses could not be obtained on both compounds due to the presence of variable amounts of dichloromethane of crystallization.

Crystal Data. 1·(CH$_2$Cl$_2$): $C_{56}H_{54}Cl_2F_3O_3P_5RuS$, M = 1190.87, orthorhombic, space group *Pna*2$_1$, a = 16.611(3), b = 27.891(6), c = 11.840(2) Å, V = 5485.3(19) Å^3, Z = 4, D_c = 1.442 g cm^{-3}, F(000) = 2440, μ(Mo-K_α) = 0.620 mm^{-1}, 150(2) K, 11326 unique reflections [R(int) = 0.0845], R (on F) = 0.0471, wR (on F^2) = 0.1154 ($I > 2\sigma I$). **2·(CH$_2$Cl$_2$):** $C_{55}H_{56}BCl_2F_6P_5Ru$, M = 1168.63, monoclinic, space group $P2_1/c$, a = 13.224(3), b = 23.865(5), c = 18.624(4) Å, β = 101.08(3)°, V = 5768(2) Å^3, Z = 4, D_c = 1.346 g cm^{-3}, F(000) = 2392, μ(Mo-K_α) = 0.557 mm^{-1}, 150(2) K, 10139 unique reflections [R(int) = 0.0538], R (on F) = 0.0535, wR (on F^2) = 0.0538 ($I > 2\sigma I$).

CCDC-670214 (for **1**) and -670215 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We gratefully acknowledge financial support from the Australian Research Council (fellowships for CJ and AS) and the EPSRC (partial studentship for CS). Thanks also go to the EPSRC Mass Spectrometry Service.

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Received: December 10, 2007
Published Online: February 21, 2008

