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Heterocyclic phosphorus ligands from cluster-bonded allenylidene

Michael I. Bruce,[a] Brian W. Skelton,[b] Allan H. White[b] and Natasha N. Zaitseva[a]

[a] *Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia*
E-mail: michael.bruce@adelaide.edu.au
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia*

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The reactions between dppm or dppe and $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ in the presence of $HBF_4{\cdot}OMe_2$ afford complexes containing novel diphosphacycloalkyne ligands, formed by double nucleophilic attack of the di-tertiary phosphine on an intermediate allenylidene complex.

There continues to be much interest in the chemistry of complexes containing unsaturated cumulenic ligands such as allenylidenes.[1] These compounds have a rich chemistry, which, by virtue of the electron deficiency of both atoms C_α and C_γ of the unsaturated carbon chain, allows the possibility of the formation of cyclic derivatives by double nucleophilic attack at these carbon atoms. These reactions have been described on several occasions in mononuclear systems, *e.g.* $[Ru(=C=C=CPh_2)(L)_2Cp']$ $[L = (CO)(PPr^i_3)$, $Cp' = Cp$; $L = PPh_3$, $Cp' = \eta^5\text{-}C_9H_7)$.[2] We report here the formation of unusual heterocyclic alkynes from allenylidene and dppm or dppe, as their Ru_3 cluster-bound complexes.

The reactions of $M_3(\mu\text{-H})\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (M = Ru, Os) with acid to give the diphenylallenylidene complexes $M_3(\mu_3\text{-}CCCPh_2)(\mu\text{-OH})(CO)_9$ were reported in 1982.[3] More recently, we have described similar reactions of $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CAr_2(OH)\}(CO)_9$ (Ar = Ph, *p*-tolyl) with dppm in the presence of $HBF_4{\cdot}OMe_2$ to give $Ru_3(\mu_3\text{-}CCCAr_2)(\mu\text{-dppm})(CO)_8$,[4] which on heating undergo aryl group-migration reactions to the allenylidene ligand.[5] Further investigations of these reactions have revealed that similar reactions with the complex derived from propyn-1-ol take a different course.

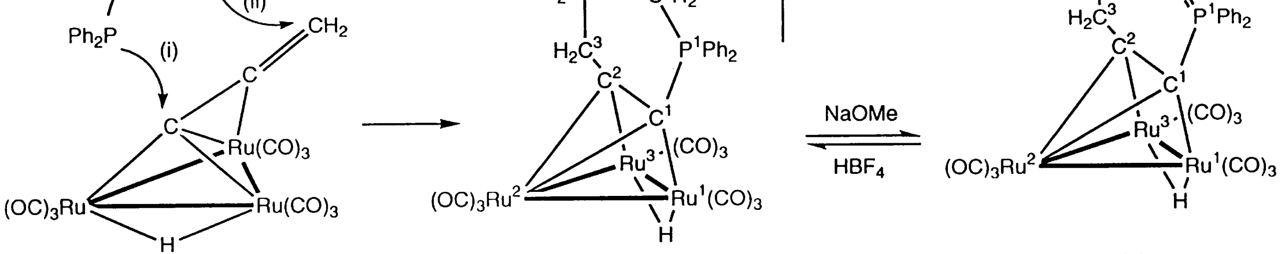
Thus, treatment of equimolar amounts of $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CH_2(OH)\}(CO)_9$ **1** and dppm with $HBF_4{\cdot}OMe_2$ afforded a bright yellow complex in 91% yield, which was shown by an X-ray study to be the salt $[Ru_3(\mu\text{-H})(\mu_3\text{-}CCPPh_2CH_2PPh_2CH_2)(CO)_9]{\cdot}[BF_4]$ **2** (Scheme 1).† Fig. 1(a) shows a plot of the cation, which contains a novel heterocyclic alkyne. The heterocycle is attached to all three atoms of the Ru_3 core by atoms C(1) and C(2) as a conventional $\mu_3\text{-}2\eta^1,\eta^2$-bonded alkyne; the other four atoms consist of P(1)–C(0)–P(2)–C(3), each phosphorus atom bearing two phenyl groups. The angle P(1)–C(0)–P(2) is 109.8(1)°. The structural study has defined two H atoms on each of C(3) and C(0). The long Ru(1)–Ru(3) vector [2.9388(5) Å] is bridged by a hydrogen atom, also located in the X-ray determination, and nine CO ligands, distributed three to each metal atom. In accord with the solid-state structure, the IR spectrum of solutions of **2** shows only terminal ν(CO) bands.‡ The ^1H NMR spectrum contains a high field doublet at δ −19.0, assigned to the cluster-bound H atom, a resonance at δ 4.67, assigned to the protons on C(3), and two double doublets at δ 4.44 and 4.87, for the PCH_2P protons.

Treatment of **2** with NaOMe generates the neutral cluster $Ru_3(\mu\text{-H})(\mu_3\text{-}CCPPh_2CHPPh_2CH_2)(CO)_9$ **3**‡ in 78% yield in a reaction that can be reversed by addition of HBF_4. Formation of **3** occurs by loss of a proton from C(0), as shown by the single crystal X-ray structure [Fig. 1(b)].† The major differences from **2** include the shortening of the P(1, 2)–C(0) distances to 1.709(3), 1.701(2) Å and concomitant opening of the P(1)–C(0)–P(2) angle to 117.3(2)°; the Ru_3 core is unchanged (average Ru–Ru separations: 2.81 Å for both). The spectroscopic properties are again consistent with the solid-state structure, with a doublet Ru–H resonance at δ −18.71 and the CH doublet at δ 3.98. The $^{31}P\{^1H\}$ NMR spectrum contains two doublet resonances at δ 4.98 and 17.76. The highest ion in the electrospray mass spectrum is at *m/z* 979, assigned to M^-.

The heterocyclic ligand in **3** contains two phosphonium ion centres, while the essentially equal P–C(0) distances and trigonal P(1)–C(0)–P(2) angle suggest that one of the formal positive charges is countered by an anionic centre in the P(1)–C(0)–P(2) system; the other is likely centred in the metal cluster. Conventional electron counting confirms that both complexes are 48-e systems, the cyclic ligand contributing six electrons.

The reaction may be extended to the formation of seven-membered heterocycles. For example, the reaction between **1** and dppe gave $Ru_3(\mu\text{-H})(\mu_3\text{-}CCPPh_2CHPPh_2CH_2CH_2)(CO)_9$, also characterised by a single-crystal X-ray structure determination (to be described elsewhere). The molecular structure is essentially the same as that of **3**, with the exception of the extra methylene group in the heterocycle.

Formation of these heterocycles, formally derived from 3,5-diphosphoniacyclohexyne and 3,6-diphosphoniacycloheptyne, respectively, is considered to proceed by nucleophilic attack



Scheme 1

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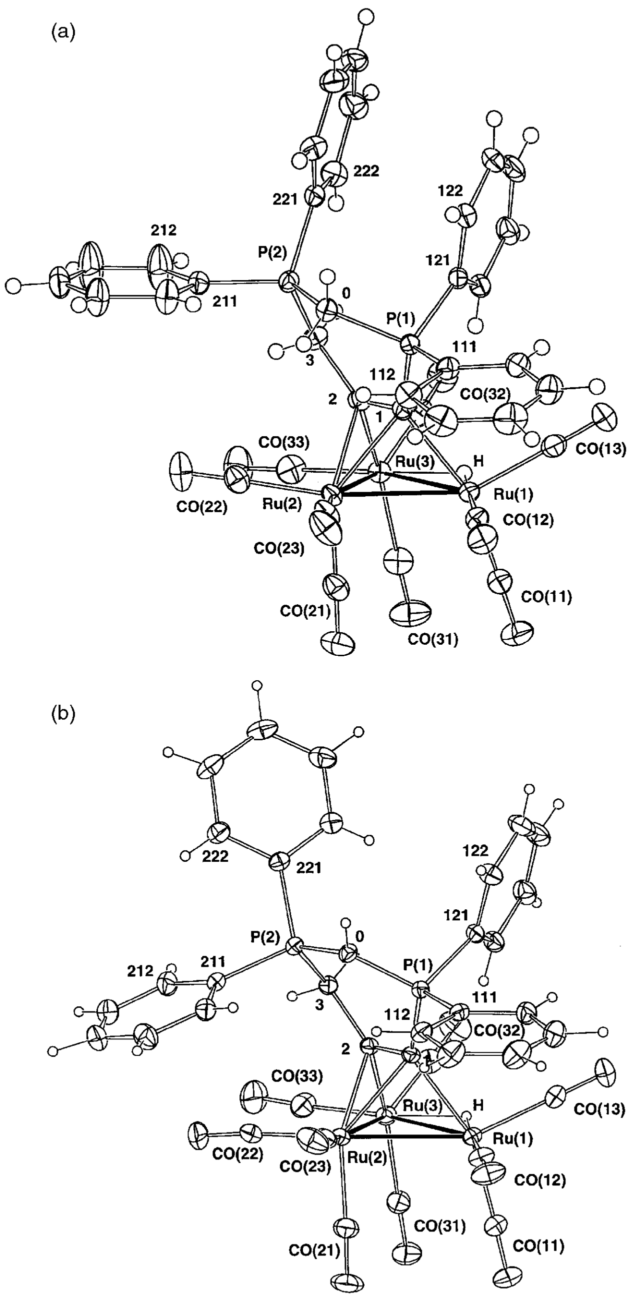

Fig. 1 Projections of the cation of **2** (a) and the molecule of **3** (b) in similar orientations, with 50 and 20% displacement ellipsoids, respectively, hydrogen atoms having an arbitrary radii of 0.1 Å. Selective geometries (**2**, **3**, respectively): Ru(1)–Ru(2) 2.7372(5), 2.7296(4); Ru(1)–Ru(3) 2.9388(5), 2.9545(4); Ru(2)–Ru(3) 2.7502(5), 2.7593(4); Ru(1)–H 1.71(3), 1.78(3); Ru(3)–H 1.80(2), 1.76(3); Ru(1)–C(1) 2.108(2), 2.105(3); Ru(2)–C(1) 2.185(3), 2.217(3); Ru(2)–C(2) 2.206(3), 2.222(3); Ru(3)–C(2) 2.077(3), 2.088(3); P(1)–C(0) 1.813(3), 1.709(3); P(1)–C(1) 1.758(3), 1.793(3); P(2)–C(0) 1.819(3), 1.701(2); P(2)–C(3) 1.828(3), 1.830(4); C(1)–C(2) 1.413(4), 1.390(4); C(2)–C(3) 1.532(4), 1.526(4) Å. P(1)–C(1)–C(2) 119.3(2), 118.0(2); C(1)–C(2)–C(3) 126.1(2), 123.9(3); C(2)–C(3)–P(2) 121.2(2), 117.5(2); C(3)–P(2)–C(0) 109.0(1), 109.4(2); P(2)–C(0)–P(1) 109.8(1), 117.3(2); C(0)–P(1)–C(1) 108.10(9), 110.9(2)°; torsion in the corresponding ring bonds being P(1)–C(1) 42.5(2), 41.4(2); C(1)–C(2) −1.6(3), −3.7(4); C(2)–C(3) −23.9(4), −36.3(4); C(3)–P(2) 3.7(2), 34.8(3); P(2)–C(0) 34.7(2), 3.5(3); C(0)–P(1) −56.6(2), −37.4(2)°.

of the bis-tertiary phosphine on a cluster-bound allenylidene ligand formed by acid-induced dehydration of the hydroxypropynyl ligand in **1**. An alternative explanation involves nucleophilic attack on the cluster-bound alkynyl group which, as previously observed, for example in reactions of Os_3-(μ-H)(μ$_3$-C_2H)$(CO)_9$ with PMe_2Ph,[6] would give a phosphinoalkyne. Subsequent attack on the protonated hydroxymethyl group by the second P centre, with elimination of water, would afford the observed product. The protonation/deprotonation reactions are examples of the complexes acting as simple acid–base systems and appear not to involve the Ru_3 cluster. It is possible that our ligands, when freed from the cluster, would isomerise to cyclic allenes related to those described recently and prepared from a phosphatriafulvene and Bu^{t}C≡P.[7] Experiments to determine this will be described in a future account, which will also define the scope of this double addition reaction [similar products are also formed from allenylidenes containing at least one hydrogen attached to C(3)] with respect to other heteroatoms.

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Notes and references

† Structure determinations. Complete spheres of CCD area-detector data (Bruker AXS instrument; $2\theta_{max} = 58°$; monochromatic Mo-Kα radiation, $\lambda = 0.71073$ Å); N_{tot} independent reflections were obtained and reduced to N_r data (R_{int} quoted), N_o [$F > 4\sigma(F)$] being used in the full-matrix least squares refinements after multiscan absorption correction, refining anisotropic thermal parameters for the non-hydrogen atoms and $(x, y, z, U_{iso})_H$ (solvent excepted, disordered in both structures). Conventional residuals R, R_w based on $|F|$ are quoted [weights: $(\sigma^2(F) = \sigma^2(I_{diff}) + 0.0004\sigma^4F^2)^{-1}$]. Computation used the XTAL 3.4 program system[8] implemented by S. R. Hall; neutral atom complex scattering factors were employed. CCDC reference numbers 153644 and 153645. See http://www.rsc.org/suppdata/dt/b1/b100661o/ for crystallographic data in CIF or other electronic format.

Crystal data for **2**: [Ru_3(μ-H)(μ$_3$-$CCPPh_2CH_2PPh_2CH_2$)$(CO)_9$]-[BF_4]·0.5CH_2Cl_2 ≡ $C_{37}H_{25}BF_4O_9P_2Ru_3 \cdot 0.5CH_2Cl_2$, $M = 1108.13$. Triclinic, $P\bar{1}$, $a = 11.3115(6)$, $b = 11.4716(7)$, $c = 17.8808(10)$ Å, $\alpha = 74.853(1)$, $\beta = 88.528(1)$, $\gamma = 63.320(1)°$, $V = 1990$ Å^3. D_c $(Z = 2) = 1.849$ g cm^{-3}. $\mu_{Mo} = 14.6$ cm^{-1}; specimen: 0.25 × 0.15 × 0.06 mm; $T_{min,max} = 0.79, 0.94$. $N_{tot} = 22008$, $N_r = 9720$ ($R_{int} = 0.020$), $N_o = 8639$, $R = 0.020$, $R_w = 0.018$. $|\Delta\rho_{max}| = 1.19(4)$ e Å^{-3}. T *ca.* 153 K.

For **3**: Ru_3(μ-H)(μ$_3$-$CCPPh_2CHPPh_2CH_2$)$(CO)_9 \cdot 0.5CH_2Cl_2$ ≡ $C_{37}H_{24}O_9P_2Ru_3 \cdot 0.5CH_2Cl_2$, $M = 1020.22$. Monoclinic, $C2/c$, $a = 25.256(2)$, $b = 11.738(1)$, $c = 27.138(1)$ Å, $\beta = 99.603(1)°$, $V = 7932$ Å^3. D_c $(Z = 8) = 1.708$ g cm^{-3}. $\mu_{Mo} = 13.3$ cm^{-1}; specimen: 0.25 × 0.18 × 0.14 mm; $T_{min,max} = 0.75, 0.93$. $N_{tot} = 47035$, $N_r = 10119$ ($R_{int} = 0.026$), $N_o = 7147$, $R = 0.033$, $R_w = 0.035$. $|\Delta\rho_{max}| = 0.80(7)$ e Å^{-3}. T *ca.* 300 K.

‡ Selected spectroscopic data for **2**: IR (CH_2Cl_2): ν(CO) 2081m, 2054s, 2018vs, 2008(sh), 1997(sh), 1983m, 1956w(br); ν(BF) 1065s cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ −19.03 [dd, 1H, *J*(HP) 3, RuH], 4.44 [dd, 1H, *J*(HH) 11, *J*(HP) 17.7, PCH_2P], 4.67 [dd, 2H, *J*(HH) 11, *J*(HP) 25.5, CH_2], 4.87 [dd, 1H, *J*(HH) 11, *J*(HP) 26 Hz, PCH_2P], 7.07–8.03 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ 4.95 [d, *J*(PP) 10.5, P(1)], 9.27 [d, *J*(PP) 10.5 Hz, P(2)]. ES MS (negative ion, *m*/*z*): 980, M^-; 952–728, $[M - n\text{CO}]^-$ (n = 1–9); 649, $[M - 2\text{H} - 9\text{CO} - \text{Ph}]^-$.

For **3**: IR (cyclohexane): ν(CO) 2069m, 2042s, 2012vs, 1998m, 1986m, 1971m, 1967(sh), 1960(sh), 1946w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ −18.71 [d, *J*(HP) 2.7 Hz, 1H, RuH], 3.98 [d, *J*(HP) 11.4 Hz, 2H, CH_2], 6.82–7.99 (m, 21H, 4 × Ph + H). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 4.98 [d, *J*(PP) 11.8 Hz], 17.76 [d, *J*(PP) 11.8 Hz]. ES MS spectrum (MeOH, negative ion, *m*/*z*): 979, M^-; 949–781, $[M - 2\text{H} - n\text{CO}]^-$ (n = 1–7); 704, $[M - 2\text{H} - 7\text{CO} - \text{Ph}]^-$.

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