Novel syntheses of heterodinuclear phosphaalkenyl complexes: X-ray structure of [Ru{P(AuPPh$_3$)=CHBu^t}Cl$_2$(CO)(PPh$_3$)$_2$]

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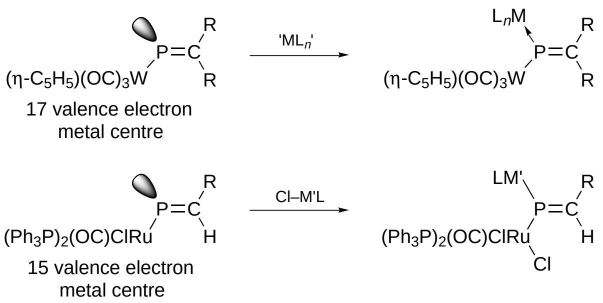
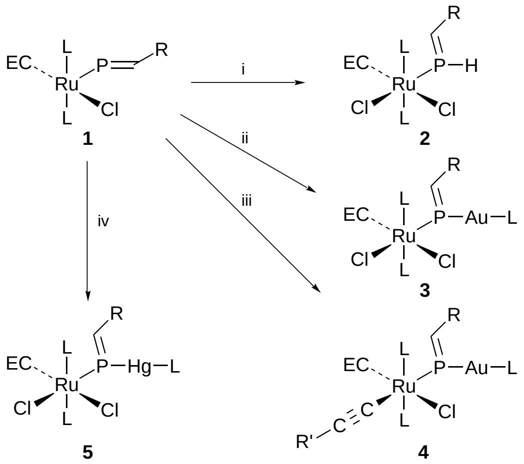
The reaction of [Ru(P=CHBu^t)Cl(CE)(PPh$_3$)$_2$] (E = O, S) with [AuX(PPh$_3$)] (X = Cl, C≡CC$_6$H$_4$Me-4), HgCl$_2$ or Hg$_2$Cl$_2$ leads *via* addition of the Au–X or Hg–Cl bonds across the Ru–P linkage to the heterodinuclear phosphaalkene complexes [Ru{P(AuPPh$_3$)=CHBu^t}ClX(CE)(PPh$_3$)$_2$] and [Ru{P(HgCl)=CHBu^t}Cl$_2$(CE)(PPh$_3$)$_2$].

Mononuclear phosphaalkenyl complexes remain rare.[1] Nevertheless, our recent observation[2] that hydroruthenation of phosphaalkynes provides an exceptionally facile entry into such compounds should presage a substantial broadening of the field. Polynuclear phosphaalkenyl complexes remain unknown, and only one example of a dinuclear complex has been structurally characterised, resulting from the reaction of the kinetically stabilised phosphaalkene ClP=C(SiMe$_3$)$_2$ with Collman's reagent.[3] The remaining examples involve the reactions of [W{P=C(R)SiMe$_3$}(CO)$_3$(η-C$_5$H$_5$)] (R = Ph, SiMe$_3$) with [Fe$_2$(CO)$_9$], [Ni(CO)$_4$] or [AuCl(PPh$_3$)].[4] In these reactions the lone pair of the phosphaalkenyl ligand coordinates to Fe(CO)$_4$, Ni(CO)$_3$ or AuCl fragments *via* a simple dative two-electron interaction. It is this aspect of phosphaalkenyl coordination chemistry with which this report is concerned, in illustrating for the first time the 1,2-addition of metal–halide and metal–carbon bonds across the P–C multiple bond of a phosphaalkenyl complex. This approach converts the three-electron phosphaalkenyl ligand into a formally neutral metallated phosphaalkene (Scheme 1). This has allowed the first structural characterisation of a heterobimetallic phosphaalkenyl complex.

The nucleophilicity of the phosphaalkenyl ligand in the complex [Ru(P=CHBu^t)Cl(CO)(PPh$_3$)$_2$] **1a** has been recently demonstrated in its reactivity with HCl to provide the phosphaalkene complex [Ru(HP=CHBu^t)Cl$_2$(CO)(PPh$_3$)$_2$] **2**.[2] Over the last decade, guided by isolobal considerations the fragment AuPPh$_3^+$ has come to be viewed as the cluster chemist's proton. Within this context, it is therefore noteworthy that the reaction of **1a** with [AuCl(PPh$_3$)] leads to the smooth and high yield conversion of **1a** to a complex formulated as [Ru{P(AuPPh$_3$)=CHBu^t}Cl$_2$(CO)(PPh$_3$)$_2$] **3a** on the basis of spectroscopic§ and crystallographic¶ data (Scheme 2, Fig. 1). Most informative amongst the spectroscopic data is the upfield shift of the ^{31}P NMR signal associated with the phosphaalkenyl ligand from δ 450.4 in **1a** to δ 319.4 in **3a**. This resonance appears as a double triplet as a result of coupling to the phosphine phosphorus nuclei bound to gold [J(PP) 268.5 Hz] and ruthenium [J(PP′) 29.6 Hz]. The former suggests an essentially *trans* P–Au–P linkage, whilst the latter is con-



Scheme 1 Phosphaalkenyl complexes as ligands; ML$_n$ = Fe(CO)$_4$, Ni(CO)$_3$, AuCl; M′L = HgCl, AuPPh$_3$



Scheme 2 (L = PPh$_3$, R = CMe$_3$, R′ = C$_6$H$_4$Me-4, E = O, S). *Reagents and conditions*: i, HCl; ii, [AuCl(L)]; iii, [Au(C≡CR′)L]; iv, Hg$_2$Cl$_2$ or HgCl$_2$.

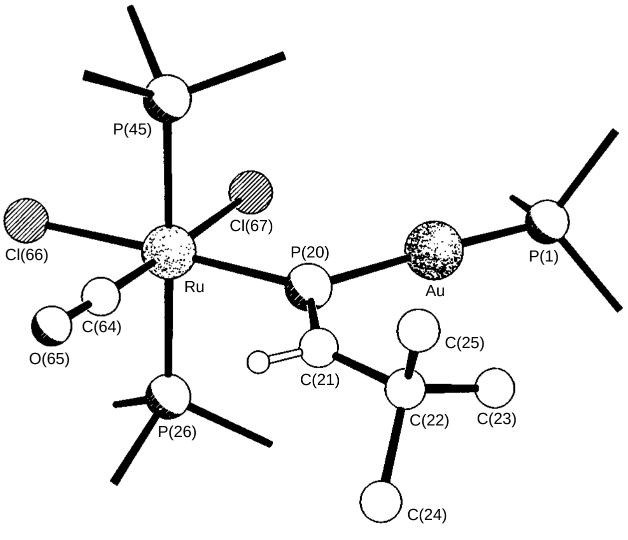


Fig. 1 Molecular geometry for [Ru{P(AuPPh$_3$)=CHBu^t)Cl$_2$(CO)(PPh$_3$)$_2$] **3a**; phenyl groups omitted

siderably larger than that found in the precursor **1a** (10.0 Hz). The resonances due to the phosphine ligands both show coupling to the phosphaalkenyl phosphorus, however there is no resolvable coupling between the phosphine resonances consistent with the absence of an Ru–Au bond.

The formulation was confirmed by a single-crystal X-ray diffraction analysis,¶ the results of which are summarised in Fig. 1. The geometry at ruthenium is essentially octahedral with *cis*-interligand angles in the range 87.2(3)–93.0(1)°, whilst the geometry at gold is close to linear [P(1)–Au–P(20) 177.6(1)°]. The two ruthenium chloride distances are 2.481(2) and 2.464(2) Å indicating that the *trans* influence of the phosphaalkenyl ligand is only marginally greater than that of the carbonyl ligand. Interest focusses on the phosphaalkenyl bridge although the novelty of **3a** leaves us with little precedent for comparison. It is noteworthy that the coordination at phosphorus is trigonal [intersubstituent angles in the range 119.7(3)–120.2(3)°], indeed this planarity extends to include Au, P(1), C(22) and the equatorial ruthenium coordination plane [maximum deviation from planarity of 0.085 Å by Cl(66)]. The P(20)–C(21) bond length of 1.664(9) Å is clearly multiple in nature, and comparable to that observed [1.640(4) Å] in $[Fe\{\mu\text{-}P{=}C(SiMe_3)_2\}_2(CO)_6]$.[3] The two Au–P distances differ only marginally, with that to the phosphaalkenyl ligand [2.320(2) Å] being the longer of the two. The Ru–P(20) separation of 2.296(2) Å is however *ca*. 0.1 Å shorter than those to the phosphines [P(45) 2.397(2), P(26) 2.413(2) Å], indicating a π-acid role for the phosphaalkenyl ligand when bound to a retrodative metal centre. Finally the *trans* disposition of the ruthenium and the butyl group about the P=C double bond confirms our earlier suggestion that hydroruthenation of $P{\equiv}CBu^t$ to provide **1a** occurs in a regiospecifically *trans* manner.

The facility of the addition of $[AuCl(PPh_3)]$ to **1a** bodes well for the future elaboration of heterobimetallic phosphaalkenyl complexes by the bridge-assisted methodology. Preliminary results indicate that the gold acetylide $[Au(C{\equiv}CC_6H_4Me\text{-}4)(PPh_3)]$ also adds across the Ru–P bond to provide the ruthenium acetylide complex $[Ru\{P(AuPPh_3){=}CHBu^t\}(C{\equiv}CC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_3]$ **4a**§ (Scheme 2). In a similar manner both mercury-(i) and -(ii) chloride react with **1** to provide $[Ru\{P(HgCl){=}PHBu^t\}Cl_2(CO)(PPh_3)_2]$ **5a**, the former reaction being accompanied by deposition of elemental mercury. Bis(alkynyl)mercurials $[Hg(C{\equiv}CR)_2]$, however, fail to react with **1a** in contrast to $[Au(C{\equiv}CC_6H_4Me\text{-}4)(PPh_3)]$. Similar reactions, and the products $[Ru\{P(AuPPh_3){=}CHBu^t\}XCl(CS)(PPh_3)_2]$ [X = Cl **3b**, $C{\equiv}CC_6H_4Me\text{-}4$ **4b**] and $[Ru\{P(HgCl){=}PHBu^t\}Cl_2(CS)(PPh_3)_2]$ **5b** are also observed between these reagents and the thiocarbonyl complex $[Ru(P{=}CHBu^t)Cl(CS)(PPh_3)_2]$ **1b**, obtained from the reaction of $[RuHCl(CS)(PPh_3)_3]$ and $P{\equiv}CBu^t$.

The chemistry described for the complexes **1** illustrates their unusual nature which makes them distinct from other phosphaalkenyl complexes for which the effective atomic number rule holds domain. For such complexes, the linear three-electron (electrophilic at P) or bent one-electron (nucleophilic at P) role of the phosphaalkenyl ligand is distinctly dichotomous. We have previously suggested[2] that the complexes **1** represent a special case: linearisation of the M=P=C linkage, and the attendant reduction of the nucleophilicity of the phosphorus is not apparently favoured by the 15-electron '$RuCl(CE)(PPh_3)_2$' fragment. Such behaviour is typical of formally isoelectronic nitrosyl complexes of the late-transition metals. This leads in the unique case of **1** to the juxtaposition of a nucleophilic phosphaalkenyl phosphorus adjacent to a coordinatively unsaturated ruthenium centre, *i.e.* a 1,2-dipole predisposed to the 1,2-addition of dipolar reagents.

We gratefully acknowledge the generous loan of ruthenium salts by Johnson Matthey Chemicals and the Nuffield Foundation and the Engineering and Physical Sciences Research Council (UK) for financial support and the provision of a diffractometer.

Footnotes

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§ *Spectral data*: for **3a**, IR/cm^{-1} (Nujol) 1950 [ν(CO)]; (CH_2Cl_2) 1960 [ν(CO)]. NMR (CD_2Cl_2, 298 K) ^{1}H: δ 0.95 (s, 9 H, Me), 7.22, 7.53, 7.99 (m × 3, 46 H, Ph + P=CH). $^{13}C\{^1H\}$: δ 199.4 [d, CO, *J*(PC) 10.7 Hz], 182.9 [d, P=C, *J*(PC) 19.6 Hz], 136–127 (Ph), 39.8 [d, CMe_3, *J*(PC) 9.0 Hz], 32.3 [d, CH_3, *J*(PC) 10.7 Hz]. $^{31}P\{^1H\}$: δ 319.4 [dt(br), P=C, *J*(PP) 268.5, *J*(PP′) *ca*. 30 Hz], 37.8 [d, $AuPPh_3$, *J*(PP) 265.8 Hz], 18.7 (d, $RuPPh_3$, *J* 29.6 Hz). FABMS: *m/z* (%) [assignment]; 1379(11) $[Ru_2Cl_2(CO)_2(PPh_3)_4]^+$, 1248(17) $[M - HCl]^+$, 1148(0.5) $[M - HP{=}CClCMe_3]$, 1188(6) $[H_2Ru_2Cl_2(CO)_2(PPh_3)_3]^+$, 987(11) $[M - HCl - PPh_3]^+$, 887(1) $[M - HP{=}CClCMe_3 - PPh_3]^+$, 689(4) $[RuCl(CO)(PPh_3)_2]^+$, 654(11) $[Ru(CO)(PPh_3)_2]^+$, 626 $[HRu(PPh_3)_2]^+$, 459(20) $[AuPPh_3]^+$, 363(8) $[RuPPh_3]^+$, 263(18) $[HPPh_3]^+$.

4a, IR/cm^{-1} (Nujol) 2094 [ν(C≡C)], 1953 [ν(CO)], 817 [δ(C_6H_4)]; (CH_2Cl_2) 2095 [ν(C≡C)], 1954 [ν(CO)]. NMR (CD_2Cl_2, 298 K) ^{1}H: δ 0.98 [s, 9 H, $C(CH_3)_3$], 2.25 [s, 3 H, $C_6H_4CH_3$], 6.79, 6.88 [(A B)$_2$, 4 H, C_6H_4, *J*(AB) 7.9 Hz], 7.55, 8.15 (m × 2, 45 H, Ph), 7.64 [d, 1 H, P=CH, *J*(PH) 23.1 Hz]. $^{13}C\{^1H\}$: δ 200.4 [d, CO, *J*(PC) 10.7 Hz], 186.3 [s(br), P=C], 135.6–126.8 (Ph and RuC≡*C*), 117.5 [d, Ru*C*≡C, *J*(PC) 19.4 Hz], 39.5 [d, CMe_3, *J*(PC) 14.3 Hz], 32.3 [d, $C(CH_3)_3$, *J*(PC) 11.1 Hz], 20.9 ($C_6H_4CH_3$). $^{31}P\{^1H\}$: δ 312.8 [dt, P=C, *J*(PP) 227.5, *J*(PP′) 27.7 Hz], 40.0 [d, $AuPPh_3$, *J*(PP) 227.5 Hz], 26.4 (d, $RuPPh_3$, 27.7 Hz). FABMS: *m/z* (%) [assignment]; 1499(2) $[M + nba - H_2O]^+$, 1470(2) $[M + nba - CO - H]^+$, 1364(0.3) $[M]^+$, 1329(2) $[M - Cl]^+$, 1248(4) $[M - HCCC_7H_7]^+$, 1118(24) $[M - HCCC_7H_7 - HPCHBu^t - CO]^+$. **5a**, IR/cm^{-1} (Nujol) 1981(sh), 1967 [ν(CO)], 1260m, 1027m, 803m; (CH_2Cl_2) 1980 [ν(CO)]. NMR (CD_2Cl_2, 298 K) ^{1}H: δ 0.85 [d, 9 H, CH_3, *J*(PH) 2.2 Hz], 7.40–7.97 (m × 4, 31 H, P=CH and Ph). $^{13}C\{^1H\}$: δ 197.3 (m, CO), 178.2 [d, P=C, *J*(PC) 26.7 Hz], 127.2–134.8 (Ph), 40.6 [d, CMe_3, *J*(PC) 14.3 Hz], 30.4 [d, CH_3, *J*(PC) 14.2 Hz]. $^{31}P\{^1H\}$: 257.9 [t, P=C, *J*(PP) 33.3, *J*(HgP) 7757 Hz], 18.2 (d, PPh_3, 27.7 Hz). FABMS: *m/z* (%) [assignment]; 1025(1) $[M - Cl]^+$, 689(14) $[RuCl(CO)(PPh_3)_2]^+$, 654(7) $[Ru(CO)(PPh_3)_2]^+$, 625(7) $[Ru(PPh_3)_2]^+$, 363(19) $[RuPPh_3]^+$.

¶ *Crystal data* for **3a**: $C_{60}H_{55}AuCl_2OP_4Ru{\cdot}2CH_2Cl_2$, $M = 1454.7$, monoclinic, space group $P2_1/n$, $a = 10.276(3)$, $b = 29.300(7)$, $c = 20.772(6)$ Å, $\beta = 101.50(2)°$, $U = 6129(3)$ Å^3, $Z = 4$, $D_c = 1.577$ g cm^{-3}, μ(Mo-Kα) = 30.4 cm^{-1}, λ = 0.710 73 Å, *F*(000) = 2896. A yellow prism of dimensions 0.83 × 0.67 × 0.27 mm was used. Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Mo-Kα radiation (ω-scans). 7949 Independent reflections were measured ($2\theta \leqslant 45°$) of which 5644 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2 using absorption-corrected data to give $R_1 = 0.047$, $wR_2 = 0.098$ for the observed data and 578 parameters. 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 182/308.

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Received, 14th October 1996; Com. 6/06987H