Carbon–Carbon Bond Formation by Reaction of an Alkyne with Ruthenium(II) Complexes. Crystal Structure of $[\overline{Ru(\eta^3\text{-}Ph_2P\text{–}CH(CPh{=}CH)\text{–}C(Bu^t){=}O})(p\text{-cymene})]PF_6$

Bénédicte Guilbert,[a] Bernard Demerseman,[a] Pierre H. Dixneuf,[a] and Carlo Mealli[b]

[a] *Laboratoire de Chimie de Coordination Organique, URA-CNRS D0415, Campus de Beaulieu, Université de Rennes, 35042 Rennes Cédex, France*

[b] *Istituto per lo Studio della Stereochemica ed Energetica dei Composti di Coordinazione del CNR, via Nardi 39, 50123 Firenze, Italy*

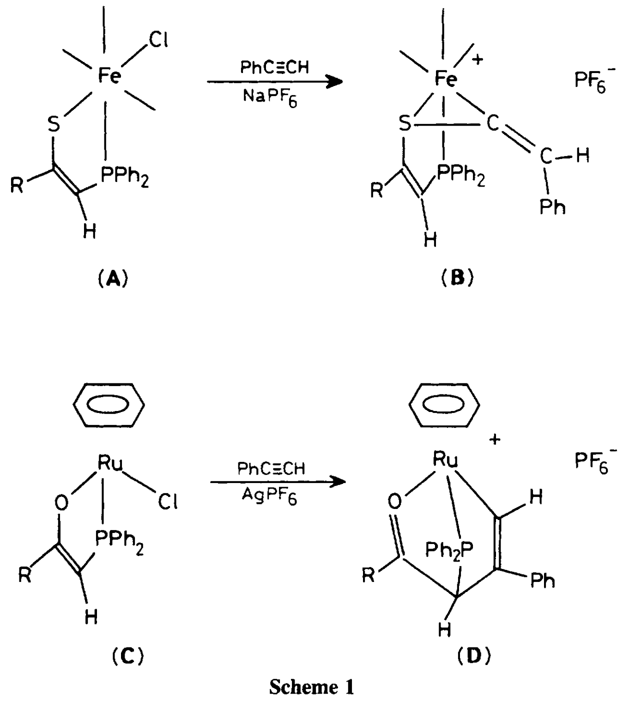
$[RuCl(\eta^2\text{-}Ph_2PCR{=}C(R')O(\eta^6\text{-arene})]$ complexes, prepared from α-diphenylphosphinoketones, react with phenylacetylene in the presence of $AgBF_4$ or $AgPF_6$ and give regioselective carbon–carbon bond formation involving the α-phosphino carbon atom of the phosphinoenolate ligand, as shown by an *X*-ray diffraction analysis.

Functional phosphines such as α-phosphino ketones or esters, owing to their bifunctional chelating capability towards metal centres, have been shown to provide efficient catalyst precursors for the telomerisation of butadiene and CO_2[1] or alkene oligomerisation.[2] In addition β-phosphinoenolato palladium (II) complexes give reversible carbon–carbon coupling of the β carbon with CO_2.[3] We have shown that β-phosphinothioenolato iron(II) complexes of type (**A**) react with terminal alkynes and lead to irreversible coupling of the sulphur atom with the electrophilic carbon of the vinylidene intermediate as in (**B**)[4] (Scheme 1).

The evidence that arene–ruthenium(II) complexes of type $(\eta^6\text{-arene})RuCl_2(PR_3)$ react with terminal alkynes to generate vinylidene ruthenium intermediate[5] has led us to prepare β-phosphinoenolato ruthenium arene derivatives for the investigation of their mode of activation of terminal alkynes. We now report the access to new $(arene)RuCl[\eta^2\text{-}Ph_2PCH{=}C(R)O]$ complexes (**C**) and their reaction with phenylacetylene. Unexpectedly a carbon–carbon coupling reaction occurs with the formation of new tripodal functional phosphine ruthenium complexes (**D**) (Scheme 1).

The air-sensitive α-diphenylphosphinoketones $Ph_2PCR^1R^2C({=}O)R^3$ (**1**) were prepared in an analogous way to that of Ph_2PCH_2COPh[6] from the corresponding lithium enolate and Ph_2PCl (Scheme 2).† The reaction of the phosphines (**1a**) and (**1b**) with $[(arene)RuCl_2]_2$ complexes at room temperature afforded the red derivatives (**2a**) and (**2b**) in good yields. On mild reaction with a base such as potassium hydroxide, or even sodium acetate, in ethanol at room temperature, deprotonation of the phosphine ligand occurred and complexes (**2a**) and (**2b**) were transformed by displacement of one chloride ligand into the corresponding η^2-diphenylphosphinoenolato ruthenium(II) derivatives (**3a**) and (**3b**). The protonation of complexes (**3**) with acids containing a non-co-ordinating anion such as HBF_4 or HPF_6 led to the cationic complexes (**4**) with retention of the η^2-co-ordinating mode of the β-ketophosphine.

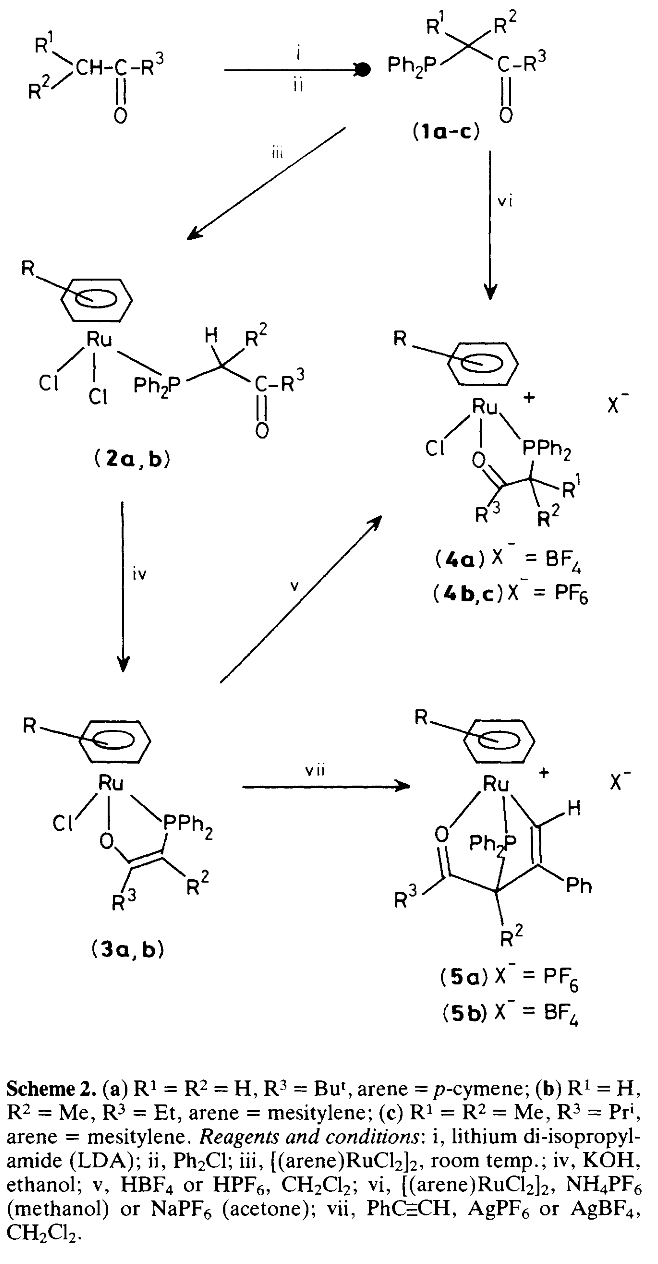
The behaviour of the phosphine (**1c**) differs significantly from that of (**1a**) and (**1b**) as no adduct of type (**2**) can be isolated. The reaction of (**1c**) with the dimeric $[(mesitylene)RuCl_2]_2$ in methanol at room temperature leads to a red solid which decomposes slowly. The i.r. spectrum of the product shows a strong band at 1600 cm^{-1} indicating the co-ordination of the ketone and the formation of a cationic complex of type (**4**). When performed in the presence of NH_4PF_6, the same reaction allows isolation of the stable, well-characterized orange salt (**4c**). This indicates an increasing co-ordinating ability of the oxygen atom of the β-ketophosphines with the introduction of methyl groups at the α carbon, leading finally to the direct substitution of a chloride ligand when phosphine (**1c**) is used.



Scheme 1

---

† All complexes reported have microanalytical and spectroscopic data in accord with their assigned structures. *Selected data*: (**1a**), m.p. 50 °C; i.r. (Nujol) ν (CO) 1690 cm^{-1}; ^1H n.m.r. ($CDCl_3$, 80 MHz) δ 7.35 (m, 10H, Ph), 3.35 (s, 2H, CH_2, $^2J_{PH}$ ~0 Hz), 1.11 (s, 9H, Bu^t); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$, 32.38 MHz) δ −20.2. (**1b**) liq., i.r. ν (CO) 1700 cm^{-1}; ^1H n.m.r. δ 7.35 (m, 10H, Ph), 3.50 (m, 1H, PCH, $^2J_{PH}$ 4.6 Hz), 2.28 (m, 2H, CH_2, $^3J_{HH}$ 7.1 Hz, $^4J_{PH}$ 2.0 Hz), 1.23 (dd, 3H, PCMe, $^3J_{PH}$ 13.4 Hz), 0.88 (t, 3H, Me); $^{31}P\{^1H\}$ n.m.r. δ −1.0. (**1c**) m.p. 100 °C; i.r. ν (CO) 1700 cm^{-1}; ^1H n.m.r. δ 7.34 (m, 10H, Ph), 3.42 (m, 1H, CH, $^3J_{HH}$ 6.6 Hz, $^4J_{PH}$ 1.7 Hz), 1.27 (d, 6H, $PCMe_2$, $^3J_{PH}$ 10.7 Hz), 1.01 (d, 6H, Me_2 of Pr^i); $^{31}P\{^1H\}$ n.m.r. δ 14.3. (**2a**) i.r. ν (CO) 1700 cm^{-1}; ^1H n.m.r. δ 4.02 (d, 2H, PCH_2, $^2J_{PH}$ 9.0 Hz), 0.66 (s, 9H, Bu^t); $^{31}P\{^1H\}$ n.m.r. δ 25.2; $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, 75.469 MHz) δ 210.8 (d, CO, $^2J_{PC}$ 11.6 Hz), 30.6 (d, PCH_2, $^1J_{PC}$ 25.8 Hz). (**2b**) i.r. ν (CO) 1710 cm^{-1}; ^1H n.m.r. δ 0.98 (dd, 3H, PCMe, $^3J_{PH}$ 15.6 Hz); $^{31}P\{^1H\}$ n.m.r. δ 29.0. (**3a**) i.r. ν (C=C) 1505 cm^{-1}; ^1H n.m.r. δ 4.32 (d, 1H, PCH=, $^2J_{PH}$ 3.2 Hz); $^{31}P\{^1H\}$ n.m.r. δ 52.6; $^{13}C\{^1H\}$ n.m.r. δ 199.6 (d, =CO, $^2J_{PC}$ 15.5 Hz), 70.5 (d, PCH=, $^1J_{PC}$ 62.7 Hz). (**3b**) i.r. ν (C=C) 1555 cm^{-1}; ^1H n.m.r. δ 1.66 (d, 3H, PCMe, $^3J_{PH}$ 9.8 Hz); $^{31}P\{^1H\}$ n.m.r. δ 66.8. (**4a**) i.r. ν (CO) 1610 cm^{-1}; ^1H n.m.r. δ 3.93 [d(AB), 2H, PCH_2, $^2J_{PH}$ 10.7 Hz, $^2J_{HH}$ 18.7 Hz]; $^{31}P\{^1H\}$ n.m.r. δ 55.9. (**4b**) i.r. ν (CO) 1625 cm^{-1}; ^1H n.m.r. δ 1.48 (dd, 3H, PCMe, $^3J_{HH}$ 7.1 Hz, $^3J_{PH}$ 11.0 Hz); $^{31}P\{^1H\}$ n.m.r. δ 77.9. (**4c**) i.r. ν (CO) 1600 cm^{-1}; $^{31}P\{^1H\}$ n.m.r. δ 76.1. (**5a**) ^1H n.m.r. δ 9.87 (dd, 1H, RuCH=, $^3J_{PH}$ 1.7 Hz, $^4J_{HH}$ 2.2 Hz), 5.68 (dd, 1H, PCH, $^2J_{PH}$ 10.3 Hz); $^{31}P\{^1H\}$ n.m.r. δ 126.6; $^{13}C\{^1H\}$ n.m.r. δ 228.6 (d, C=O, $^2J_{PC}$ 5.9 Hz), 166.2 (d, RuCH=, $^2J_{PC}$ 14.4 Hz), 137.3 (d, =CPh, $^2J_{PC}$ 10.6 Hz), 66.4 (d, PCH, $^1J_{PC}$ 32.0 Hz). (**5b**) ^1H n.m.r. δ 8.91 (d, 1H, RuCH=, $^3J_{PH}$ 2.9 Hz); $^{31}P\{^1H\}$ n.m.r. δ 144.9; $^{13}C\{^1H\}$ n.m.r. δ 225.8 (d, C=O, $^2J_{PC}$ 7.6 Hz), 172.2 (d, RuCH=, $^2J_{PC}$ 14.4 Hz), 141.0 (d, =CPh, $^2J_{PC}$ 16.6 Hz), 75.0 (d, PC, $^1J_{PC}$ 26.8 Hz).



Scheme 2. (**a**) $R^1 = R^2 = H$, $R^3 = Bu^t$, arene = *p*-cymene; (**b**) $R^1 = H$, $R^2 = Me$, $R^3 = Et$, arene = mesitylene; (**c**) $R^1 = R^2 = Me$, $R^3 = Pr^i$, arene = mesitylene. *Reagents and conditions*: i, lithium di-isopropylamide (LDA); ii, Ph_2Cl; iii, $[(arene)RuCl_2]_2$, room temp.; iv, KOH, ethanol; v, HBF_4 or HPF_6, CH_2Cl_2; vi, $[(arene)RuCl_2]_2$, NH_4PF_6 (methanol) or $NaPF_6$ (acetone); vii, $PhC{\equiv}CH$, $AgPF_6$ or $AgBF_4$, CH_2Cl_2.

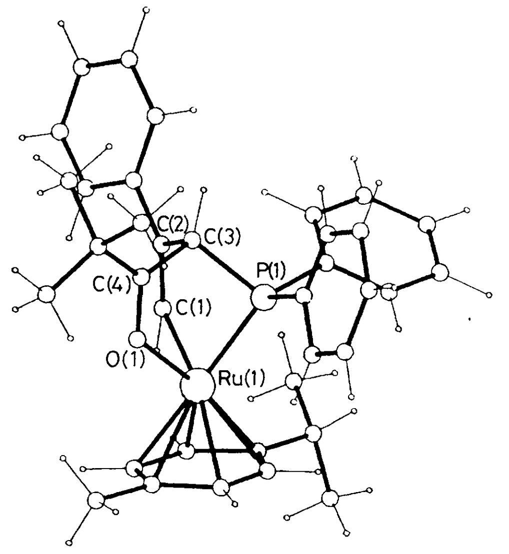


Figure 1. Molecular structure of $[Ru\{\eta^3\text{-}Ph_2PCH(CPh{=}CH)C(Bu^t){=}O\}(p\text{-cymene})]\ PF_6$ (**5a**). Selected bond distances (Å) and angles (°) are: Ru–O(1) 2.12(1), Ru–C(1) 2.03(2), Ru–P(1) 2.293(5), C(1)–O(1) 1.24(2), C(1)–C(2) 1.36(2), Ru–C(arene) 2.23(3) (average); P(1)–Ru–C(1) 77.5(5), P(1)–Ru–O(1) 77.6(3), C(1)–Ru–O(1) 82.5(6), Ru–C(1)–C(2) 120(1), Ru–O(1)–C(1) 120(1).

As β-phosphinothiolatoiron(II) complexes (**A**) were shown[4] to activate terminal alkynes *via* a metal–vinylidene species and give a carbon–sulphur bond formation (**B**) (Scheme 1), the mode of activation of phenylacetylene by the isoelectronic complexes (**3**) was investigated. Complexes (**3a**) and (**3b**) reacted in dichloromethane with phenylacetylene in the presence of one equivalent of $AgBF_4$ or $AgPF_6$ for 12 h at room temperature, or alternatively, but with a lower yield in methanol, in the presence of NH_4PF_6. Orange crystalline complexes (**5a**) and (**5b**) were isolated. Although no strong carbonyl absorption in the i.r. was present, the $^4J_{HH}$ coupling constant value of 2.2 Hz for (**5a**) rules out a structure of type (**B**) and is consistent with a structure of type (**D**) (Scheme 1).

The structure of complex (**5a**) was determined by a single crystal *X*-ray analysis. In the complex cation (Figure 1) a formal Ru^{II} metal attains the 18e configuration by co-ordination of an arene ligand and of a newly formed tripodal ligand carrying three different donor functions, *i.e.* a phosphine, a σ-co-ordinated vinyl fragment, and an oxygen atom of a keto group.‡ In particular the Ru–O [2.12(1) Å] and Ru–C [2.03(2) Å] bonds, relative to the latter two donating groups, compare well with Ru–O [2.11(2) Å] in $Ru(CO)[C_6H_4MeC(O)C_6H_4Me]Cl(PMe_2Ph)_2$[7] and Ru–C [2.06(1) Å] in $Ru[CH{=}C(Me)C(O)(OC_4H_9)](H)(PPh_3)_3$.[8] The formation of complexes (**5**) with a structure of type (**D**) is likely the result of a C–C intramolecular coupling reaction of the nucleophilic α carbon of the chelate phosphinoenolate ligand with the substituted carbon atom of the η^2-co-ordinated alkyne.

The formation of complexes (**5**) contrasts not only with the formation of an iron vinylidene intermediate leading to (**B**) but also with the observation that complexes of type $RuCl_2(PR_3)$(arene), analogous to derivatives (**3**), lead to the formation of carbene ruthenium complexes by reaction with terminal alkynes, *via* the initial co-ordination of the alkyne and its rapid rearrangement into a ruthenium vinylidene intermediate.[5] The present results seem consistent with a fast carbon–carbon coupling reaction of the alkyne and that the chelation of the phosphinoenolate ligand disfavours the η^2-alkyne → η^1-vinylidene rearrangement at the metal centre.

---

‡ *Crystal data*: $C_{36}H_{40}P_2O_1F_6Ru_1$, monoclinic, $P2_1/n$, $a = 14.870(4)$, $b = 20.087(6)$, $c = 12.454(5)$ Å, $\beta = 92.67(3)$°, $U = 3715.9$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}. Data collected on a Philips PW 1100 diffractometer with Mo-K_α radiation [3780 measured ($2\theta \leq 40$°), 2047 used ($I \geq 3\sigma_I$) reflections]. The structure was solved by Patterson methods and refined to $R = 0.079$ ($R_W = 0.075$). Rigid body refinement was used for the phenyl rings (but not the arene ring). Anisotropic temperature factors were used only for the Ru and P atoms. The hydrogen atoms were introduced at calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank Johnson–Matthey Chemicals Limited for a loan of ruthenium trichloride.

Received, 29th March 1989; Com. 9/01313J

References

1 P. Braunstein, D. Matt, and D. Nobel, *J. Am. Chem. Soc.*, 1988, **110**, 3207.

2 W. Keim, A. Behr, B. Kruber, B. Hoffmann, F. H. Kowaldt, V. Kürschner, B. Limbäcker, and F. P. Sistig, *Organometallics*, 1986, **5**, 2356, and references therein.

3 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.

4 A. Samb, B. Demerseman, P. H. Dixneuf, and C. Mealli, *J. Chem. Soc., Chem. Commun.*, 1988, 1408.

5 K. Ouzzine, H. Le Bozec, and P. H. Dixneuf, *J. Organometal. Chem.*, 1986, **317**, C25.

6 S. E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt, and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.

7 R. J. Dauter, R. Mawby, C. D. Reynolds, and D. R. Saunders, *J. Chem. Soc., Dalton Trans.*, 1985, 1235.

8 S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 3874.