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Novel insertion of ethynylbenzene derivatives bearing an electron-withdrawing substituent at the 4-position into a P–C bond and their transannular insertion between a metal atom and an *ipso*-carbon atom of the phosphine ligand†

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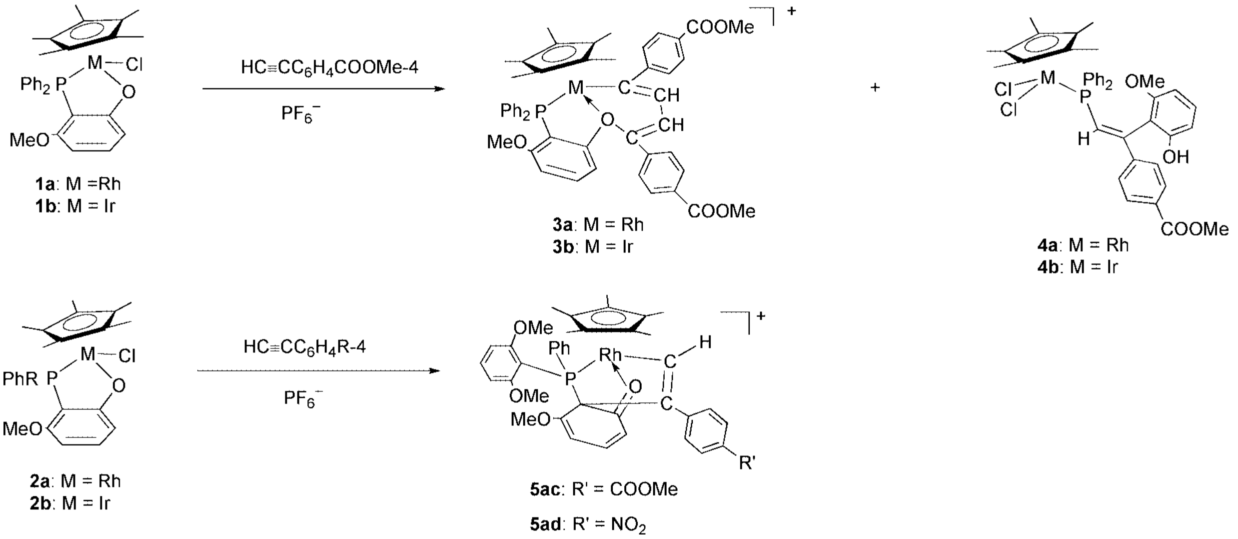
Reactions of Cp*MCl(P–O) (M = Rh, Ir) bearing P–O coordination with ethynylbenzene derivatives having an electron-withdrawing group in the presence of a PF_6 anion result in either insertion into a P–C bond or a transannular addition between a metal and an *ipso*-carbon of the phosphine.

When transition metal halide complexes are allowed to react with alkynes in the presence of anions such as PF_6^-, BF_4^-, *etc.*, it is well-known that vinylidene or carbene complexes may be formed, depending on the solvent.[1] However, we have recently reported that the unprecedented insertion of alkyne into a metal–oxygen σ-bond can occur without the formation of vinylidene complexes.[2] On treatment of the rhodium complex [Cp*RhCl(MDMPP-κ^2*P*,*O*)] **1a** (MDMPP-κ^2*P*,*O* = κ*O*-1-*O*-κ*P*-2-PPh$_2$-3-MeOC$_6$H$_3$) with mono- and di-substituted alkynes (HC≡CPh, HC≡CCOOR or ROOCC≡CCOOR; R = Me, Et) in the presence of the PF_6^- anion, single and double insertion of alkynes into the Rh–O bond occurred to form various types of complex, depending on the alkyne, as follows; (1) a complex bearing five- and six-membered rings arising from a double insertion, (2) a seven-membered metallacycle bearing a CO ligand arising from a single insertion and an extraction of CO from an ester and (3) a neutral complex bearing a seven-membered ring arising from a single insertion.[2]

When ethynylbenzene derivatives bearing an electron-withdrawing substituent at the 4-position of the phenyl group were treated with [Cp*MCl(MDMPP-κ^2*P*,*O*)] (**1a**: M = Rh;[3] **1b**: M = Ir[4]) or [Cp*RhCl(BDMPP-κ^2*P*,*O*)] **2a**[5] (BDMPP-κ^2*P*,*O* = κ*O*-1-*O*-κ*P*-2-PRPh-3-MeOC$_6$H$_3$) bearing a *P*,*O* bidentate ligand derived from (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) and bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) in the presence of KPF$_6$, we found that novel types of reaction: an insertion into a P–C bond or a transannular addition between a Rh atom and an *ipso*-carbon atom of the phosphine ligand, occurred readily. We report here the reactions with ethynylbenzene derivatives bearing an electron-withdrawing substituent such as the COOMe or NO$_2$ group.

Reaction of **1a** with HC≡CC$_6$H$_4$COOMe-4 at room temperature in the presence of KPF$_6$ in acetone–CH$_2$Cl$_2$ gave two compounds by crystallization from CH$_2$Cl$_2$–diethyl ether: **3a**‡ and **4a**‡ as confirmed from elemental analyses and FAB mass spectroscopy (Scheme 1). X-Ray analysis revealed that **3a** contained a (P,O,C) tridentate ligand resulting from the head-to-head double-insertion of alkyne into the Rh–O bond.§ Two carbon atoms bearing the phenyl group were connected to the Rh and O atoms. The infrared spectrum showed bands due to methoxycarbonyl and PF$_6$ groups at 1717 and 839 cm^{-1}, respectively. The ^{1}H NMR spectrum in CD$_2$Cl$_2$ showed one doublet at δ 1.36 due to the Cp* protons and three singlets at δ 3.35, 3.88 and 3.95; the former is due to the methoxy group and the others are due to the methoxycarbonyl groups. The ^{31}P{^{1}H} NMR spectrum showed a doublet at δ 35.84 (J_{RhP} = 157.8 Hz).

The infrared spectrum of **4a** showed three characteristic bands at 3285, 1717 and 1605 cm^{-1} due to the OH, carbonyl groups and C–C double bond, respectively. In the ^{1}H NMR spectrum a broad resonance due to a hydroxyl proton, which



Scheme 1 Reactions of **1** and **2** with HC≡CC$_6$H$_4$R′-4 (R = 2,6-(MeO)$_2$C$_6$H$_3$, R′ = COOMe or NO$_2$).

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† Electronic supplementary information (ESI) available: spectroscopic data for complexes **3**–**5**. See http://www.rsc.org/suppdata/dt/b0/b004984k/

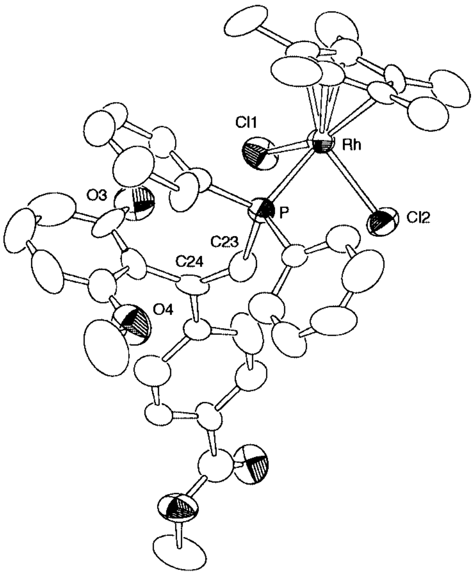

Fig. 1 Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.341(5), Rh(1)–Cl(1) 2.428(5), Rh(1)–Cl(2) 2.411(5); P(1)–C(23) 1.83(2), C(23)–C(24) 1.32(2); P(1)–Rh(1)–Cl(1) 87.1(2), P(1)–Rh(1)–Cl(2) 85.0(2), Cl(1)–Rh(1)–Cl(2) 93.4(2), P(1)–C(23)–C(24) 135(1), C(23)–C(24)–C(25) 117(1).

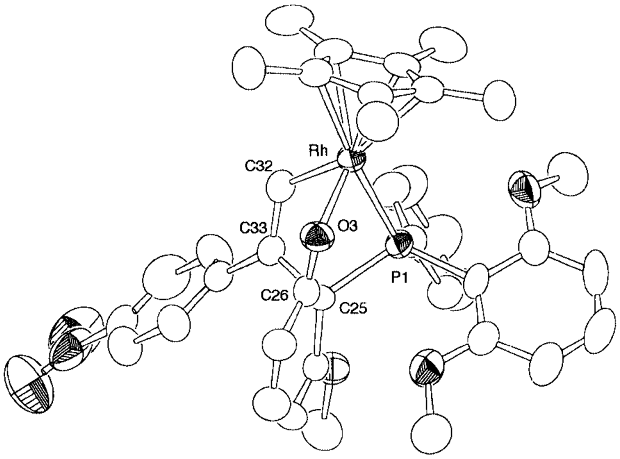

Fig. 2 Molecular structure of **5ad**. Selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.304(2), Rh(1)–O(3) 2.106(4), Rh(1)–C(32) 2.013(6), O(3)–C(26) 1.263(7), C(25)–C(26) 1.505(8), P(1)–C(25) 1.943(6), C(25)–C(33) 1.567(8), C(32)–C(33) 1.340(8); P(1)–Rh(1)–O(3) 81.1(1), P(1)–Rh(1)–C(32) 76.3(2), O(3)–Rh(1)–C(32) 85.2(2), Rh(1)–P(1)–C(25) 90.2(2), P(1)–C(25)–C(26) 105.1(4), C(25)–C(26)–O(3) 118.7(5), Rh(1)–O(3)–C(26) 117.9(4), Rh(1)–C(32)–C(33) 120.4(4), C(32)–C(33)–C(25) 114.2(5), P(1)–C(25)–C(33) 96.4(4).

disappeared on treatment with D_2O, appeared at δ 6.74 in addition to three characteristic methyl resonances at δ 1.41(d), 3.44(s) and 3.83(s), due to 1,2,3,4,5-pentamethylcyclopentadienyl, methoxy and methoxycarbonyl groups, respectively. There were no signs of a PF_6 group in the infrared and $^{31}P\{^1H\}$ NMR spectra, suggesting that the complex was neutral. The structure was confirmed by X-ray analysis (Fig. 1).¶ As expected, the molecule is neutral and the rhodium atom is surrounded by two chlorine atoms and one phosphorus atom. *Cis*-insertion of alkyne into the P–C bond has occurred, accompanied by cleavage of a Rh–O bond. The Rh–P bond length of 2.341(5) Å is longer than that of **1a** by 0.04 Å, due to the absence of chelation and is 0.02 Å shorter than that (2.366(1) Å) of Cp*$RhCl_2$(MDMPP), probably due to lower steric demand than in the MDMPP ligand.[3] A similar reaction occurred on treatment with **1b** in acetone–CH_2Cl_2 to give **3b** and **4b** (Scheme 1).‡ The fact that a similar reaction in MeOH gave exclusively **3a** as the only isolated complex confirmed that the chlorine atom in **4** originated from dichloromethane.

Complex **2a** containing the bulky phosphine BDMPP was treated with $HC\equiv CC_6H_4R$-4, (R = COOMe or NO_2) in acetone–CH_2Cl_2 in the presence of KPF_6 at room temperature (Scheme 1) to yield complexes **5ac** (yellow, R = COOMe) and **5ad** (brown, R = NO_2) as confirmed from elemental analyses and FAB mass spectroscopy.‡ X-Ray analysis of **5ad** revealed that the structure consists of five- and six-membered rings derived from a transannular insertion of alkyne between the Rh atom and the *ipso*-carbon atom of the phosphine ligand, accompanying the subsequent transformation of the Rh–O σ-bond to a Rh←O coordination (Fig. 2).|| The change of this bonding mode caused an elongation of *ca.* 0.06 Å in the Rh–O bond length.

The IR spectrum showed bands due to methoxycarbonyl and ketone groups at 1715 and 1630 cm^{-1} for **5ac** and due to a ketone group at 1628 cm^{-1} for **5ad**, respectively. The ^1H NMR spectrum showed three methoxy groups at δ 2.97 (s), 3.06 (bs) and 3.49 (bs) and one methoxycarbonyl group at δ 3.84 (s) for **5ac** and three methoxy groups at δ 2.99 (s), 3.08 (bs) and 3.52 (bs) for **5ad**, respectively. A remarkable feature is that the $^{31}P\{^1H\}$ NMR doublets show large downfield shifts (*ca.* δ 140). Further mechanistic studies are now in progress.

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Notes and references

‡ Elemental analyses of all new complexes prepared here are in good agreement with the calculated values. Elementary analyses and spectroscopic data are enclosed in the electronic supplementary information.†

§ Crystal data for **3a**: $C_{49}H_{47}O_6P_2F_6Rh$, M = 1010.8, monoclinic, space group $P2_1/a$ (no. 14), a = 15.534(3) Å, b = 19.986(3) Å, c = 15.757(3) Å, β = 103.70(1)°, V = 4752(1) $Å^3$, Z = 4, D = 1.413 g cm^{-3}, μ = 4.96 cm^{-1} (MoKα), F(000) = 2072, T = 298 K. Data were collected on a Rigaku AFC5S difractometer. The structure was solved by Patterson methods, and non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R1$ = 0.064 for 3298 reflections and R_w = 0.198 for 8328 reflections.

¶ Crystal data for **4a**: $C_{39}H_{42}O_6PCl_2Rh$, M = 811.5, orthorhombic, space group $Pca2_1$ (no. 29), a = 34.835(7) Å, b = 9.135(8) Å, c = 12.305(5) Å, V = 3915(5) $Å^3$, Z = 4, D = 1.377 g cm^{-3}, μ = 6.55 cm^{-1} (MoKα), F(000) = 1672, T = 300 K. The structure was solved by Patterson methods, and non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R1$ = 0.068 for 2216 reflections and R_w = 0.203 for 3607 reflections.

|| Crystal data for **5ad**: $C_{39}H_{46}NO_9P_2F_6Rh$, M = 951.6, monoclinic, space group $P2_1/a$ (no. 14), a = 15.299(7) Å, b = 14.826(7) Å, c = 19.505(9) Å, β = 106.78(3)°, V = 4235(3) $Å^3$, Z = 4, D = 1.492 g cm^{-3}, μ = 5.57 cm^{-1} (MoKα), F(000) = 1952, T = 298 K. The structure was solved by Patterson methods, and non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R1$ = 0.065 for 4458 reflections and R_w = 0.180 for 7708 reflections. CCDC reference number 186/2117. See http://www.rsc.org/suppdata/dt/b0/b004984k/ for crystallographic files in .cif format.

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