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Novel single or double insertion of alkynes into rhodium– and iridium–oxygen or –phosphorus atom bonds and transannular addition of 1-alkynes between the rhodium atom and the *ipso*-carbon atom of the phosphorus ligand

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Reactions of Cp*MCl(MDMPP-*P*,*O*) (**1a**: M = Rh; **1b**: M = Ir; MDMPP-*P*,*O* = *P*Ph$_2$(C$_6$H$_3$-2-MeO-6-*O*)) or Cp*MCl(BDMPP-*P*,*O*) (**2a**: M = Rh; **2b**: M = Ir; BDMPP-*P*,*O* = *P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-*O*)) with 1-alkynes were carried out in the presence of KPF_6. Complex **1a** reacted with HC≡CR (R = Ph, *p*-tolyl) to give [Cp*Rh{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*-CR=CHCH=*C*R))}](PF$_6$) **5** bearing the (*P,O,C*) tridentate ligand derived from a head-to-head dimerization of 1-alkynes, whereas reaction with *n*BuC≡CH gave a head-to-tail double insertion complex **6**, however the reactiones of **1b** in MeOH gave carbene complexes [Cp*Ir{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-*O*)-(=C(OMe)CH$_2$R)}](PF$_6$) **13** and a carbonyl complex [Cp*Ir(CO){*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-*O*)}](PF$_6$) **14**. Rhodium complexes **1a** and **2a** afforded [Cp*Rh(CO){*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*CH=*C*(COOR)))}](PF$_6$) **8** or [Cp*Rh(CO)-{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(*O*CH=*C*(COOR)))}](PF$_6$) **11** on treatment with HC≡CCOOR (R = Me, Et). Reactions of **1a**, **1b**, **2a** or **2b** with ROOCC≡CCOOR (R = Me, Et) gave [Cp*MCl{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}] (**9**: M = Rh, **17**: M = Ir) and [Cp*MCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}] (**12**: M = Rh, **18**: M = Ir), respectively. Reactions of **1a** or **1b** with HC≡CC$_6$H$_4$-4-COOMe bearing an electron-withdrawing substituent gave the head-to-head double insertion products (**5c**: M = Rh; **16**: M = Ir) and Cp*MCl$_2$[*P*Ph$_2${CH=C(C$_6$H$_3$-4-COOMe)(C$_6$H$_3$-2-(MeO)-6-(OH))}] (**7**: R = Rh; **15**: R = Ir), and resulted in a *cis*-insertion into the P–C bond of the phosphine ligand and a cleavage of the Rh–O bond. Reaction with **2a** afforded **10a**, derived from a transannular addition of 1-alkyne between the Rh atom and the *ipso*-carbon atom of the phosphine ligand. Reactions of **9** with CO or isocyanides (L) in the presence of KPF_6 or Ag(CF$_3$SO$_3$) gave [Cp*Rh(L){*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}]X (L = XylNC, MesNC, CO; X = PF$_6$, CF$_3$SO$_3$). Structural data for some complexes obtained here are described. The reaction mechanism is discussed.

Introduction

Metal alkynyl complexes are currently of great interest[1,2] since they can be used as valuable synthons for constructing vinylidene or carbene complexes for use in organic synthesis.[3–8] Reactions of organotransition metal halides with 1-alkynes in the presence of anions such as PF_6^-, BF_4^-, and $CF_3SO_3^-$, are representative among the preparative methods of vinylidene complexes.[9] One *ortho*-methoxy group in (2,6-dimethoxyphenyl)diphenylphosphine can be demethylated in the reaction with isoelectronic complexes [Cp*MCl$_2$]$_2$ (M = Rh or Ir; Cp* = pentamethylcyclopentadienyl) or [(η^6-arene)RuCl$_2$]$_2$ (η^6-arene = C$_6$Me$_6$, *p*-cymene, C$_6$H$_3$Me$_3$), giving corresponding metal complexes with a (*P*,*O*) chelating phosphine, (η^6-arene)Ru-Cl(MDMPP-*P*,*O*)[10,11] or Cp*MCl(MDMPP-*P*,*O*)[12,13] (Cp* = C$_5$Me$_5$; MDMPP-*P*,*O* = *P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-*O*)). We have recently reported the unprecedented insertion of tcne (or tcnq) into the C–H bond adjacent to the M–O bonds, producing Cp*-MCl[*P*Ph$_2${C$_6$H$_2$-2-(MeO)-5-(C(CN)$_2$C(CN)$_2$H)-6-*O*}] when the aforementioned rhodium(III) and iridium(III) complexes were treated with tcne or tcnq.[14]

We have also reported that treatment of the ruthenium(II) complex with PhC≡CH in the presence of $NaPF_6$ in a mixture of acetone and CH_2Cl_2, afforded a vinylidene complex, [(η^6-C$_6$Me$_6$)Ru(MDMPP-*P*,*O*)(=C=CHPh)](PF$_6$).[15] This reaction is one of the well known preparative methods for vinylidene complexes.[9] However, the treatment of Cp*RhCl(MDMPP-*P*,*O*) **1a**[12] with 1-alkynes such as HC≡CCOOMe, PhC≡CH and *n*BuC≡CH, and disubstituted alkynes such as C$_2$(CO$_2$R)$_2$ (R = Me, Et) in the presence of $NaPF_6$ or KPF_6 led to unusual reactions; in the reaction with HC≡CCOOMe, an extraction of CO from an ester group and the insertion of another 1-alkyne into an Rh–O σ-bond occurred, producing a seven-membered metallacycle, and reactions with HC≡CR (R = Ph, *n*Bu) led to the formation of complexes bearing five- and six-membered rings accompanying a double insertion of 1-alkynes into an Rh–O σ-bond. Treatment with disubstituted alkynes also led to a single insertion into a Rh–O σ-bond. A similar insertion of unsaturated molecules into the metal–oxygen bond of platinum alkoxides has been achieved with perfluoro-olefins[16] such as CF_2=CF_2 and hexafluorocyclobutene. In this study, the insertion of alkyne into the transition metal–O σ-bonds is performed for the first time.[17,18] These unprecedented reactions allow control of single and double insertion of alkynes into the metal–O bond of pentamethylcyclopentadienyl-rhodium and –iridium complexes bearing the (P,O) bidentate ligands by variation of the alkyne substituents.

Part of this work has already been published.[19,20]

Results and discussion

Reactions of [Cp*RhCl$_2$]$_2$ with (2,6-dimethoxyphenyl)diphenylphosphine or bis(2,6-dimethoxyphenyl)phenylphosphine

We previously reported that the reaction of [Cp*RhCl$_2$]$_2$ with PPh$_2$(C$_6$H$_3$-2,6-(MeO)$_2$) at room temperature gave Cp*RhCl$_2$-

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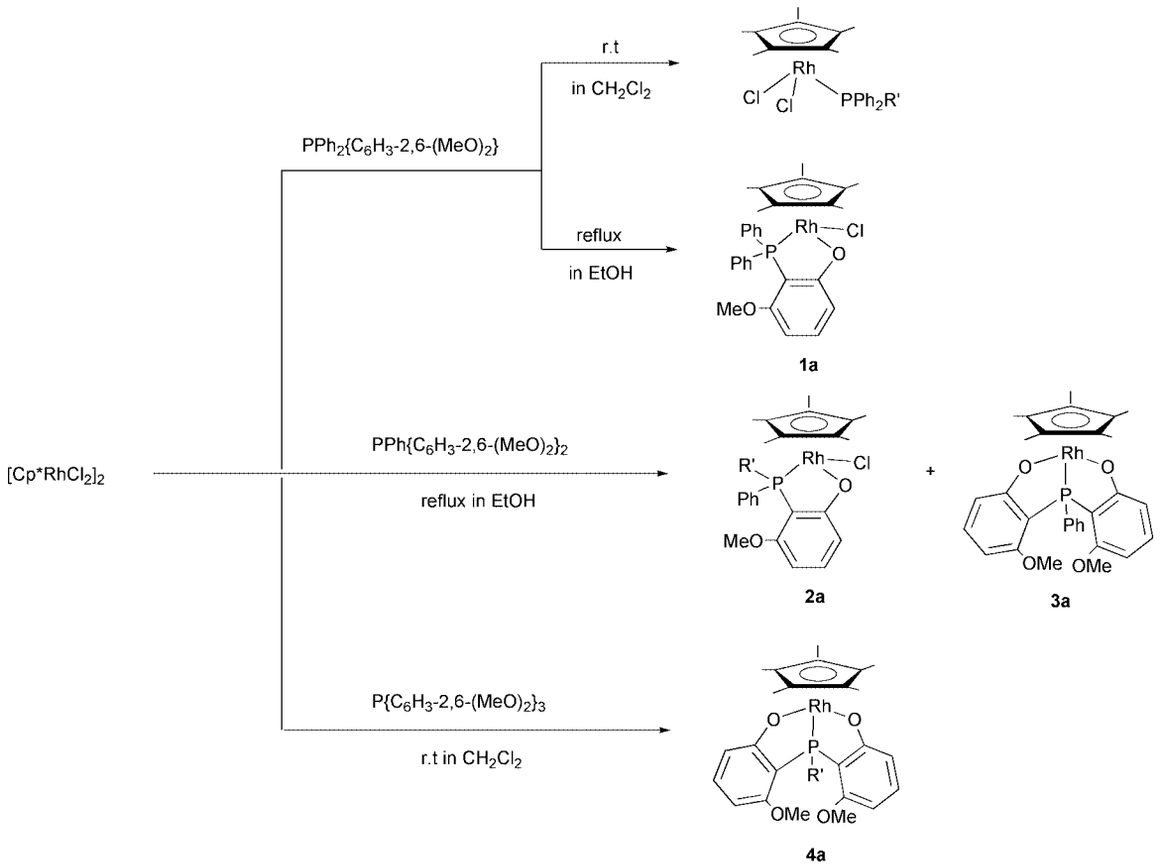


Scheme 1 Reactions of $[Cp^*RhCl_2]_2$ with (2,6-dimethoxyphenyl)diphenylphosphine, bis(2,6-dimethoxyphenyl)phenylphosphine or tris(2,6-dimethoxyphenyl)phosphine (R′ = 2,6-$(MeO)_2C_6H_3$).

{*P*Ph_2(C_6H_3-2,6-$(MeO)_2$)} in high yield, whereas the reaction at reflux in EtOH resulted in demethylation of the phosphine forming Cp*RhCl(MDMPP-*P*,*O*) **1a**, showing a bidentate *P*,*O* coordination.[12] In this study, a mixture of $[Cp^*RhCl_2]_2$ and bulky bis(2,6-dimethoxyphenyl)phenylphosphine was heated in EtOH, causing the demethylation of one or two methyl groups of the phosphine and giving two orange complexes, [Cp*RhCl(BDMPP-*P*,*O*)] **2a** (BDMPP-*P*,*O* = *P*Ph{C_6H_3-2,6-$(MeO)_2$}{C_6H_3-2-(MeO)-6-*O*}) and [Cp*Rh{*P*Ph(C_6H_3-2-(MeO)-6-*O*)$_2$}] **3a** as separated by chromatography on deactivated alumina (containing 10% H_2O) (Scheme 1).

It was confirmed by X-ray analysis that **2a** consists of a Rh_RP_R/Rh_SP_S pair (Fig. 1). Diastereomers could in principle exist in **2a** which has two chiral centers, however the ^{1}H NMR spectra revealed that **2a** consists of only the one diastereomer at room temperature and at −60 °C, exhibiting one doublet at δ 1.34 due to pentamethylcyclopentadienyl protons. The methoxy protons appeared at δ 3.08, 3.25 and 3.74 as sharp singlets. The inequivalence for the methoxy protons is assumed to arise from either the presence of a chiral center of the P atom or restricted rotation of the $C_6H_3(OMe)_2$ ring about the P–C axis.

It has been reported that the complexes (η^6-arene)RuCl(BDMPP-*P*,*O*) (η^6-arene = 1,2,3,4-$Me_4C_6H_2$ *p*-cymene, 1,3,5-$Me_3C_6H_3$) derived from the reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ with PPh{(C_6H_3-2,6-$(MeO)_2$}$_2$ exist as two diastereomers in solutions and as a Ru_RP_R/Ru_SP_S pair in the solid state.[10,11] It was found that reaction with bulky tris(2,6-dimethoxyphenyl)-phosphine, P{C_6H_3-2,6-$(MeO)_2$}$_3$, readily induced demethylation of the two methyl groups even at room temperature, affording Cp*Rh{*P*(C_6H_3-2,6-$(MeO)_2$)(C_6H_3-2-(MeO)-6-*O*)$_2$} **4a** containing a P,O,O′-tridentate ligand. The ^{1}H NMR spectrum indicated two singlets at δ 3.42 and 3.49 due to methoxy protons. The detailed structure of **4a** was confirmed by X-ray analysis (Fig. 2). The degree of demethylation decreased with decrease of bulkiness of the phosphine ligand.

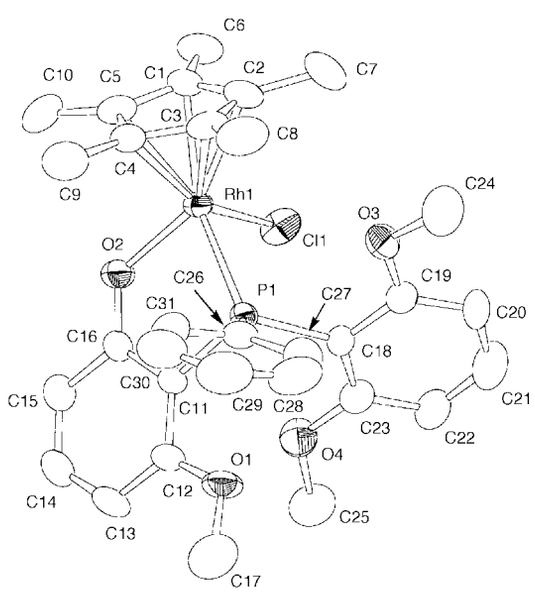


Fig. 1 Molecular structure of **2a**; thermal ellipsoids are drawn to encompass 50% probability.

Similar reactive behavior has been noted in the reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ with these phosphines.[10,11]

Reactions of [Cp*RhCl(MDMPP-*P*,*O*)] 1a with alkynes

Reaction of **1a** with an excess of ethynylbenzene or ethynyltoluene in the presence of KPF_6 or $NaPF_6$ at room temperature gave orange complexes [Cp*Rh{*P*Ph_2(C_6H_3-2-(MeO)-6-(*O*CR=CHCH=*C*R))}](PF_6) (**5a**: R = Ph; **5b**: R = 4-tolyl) (Scheme 2). X-Ray analyses of **5a**[19] and **5b** revealed that a Rh atom is surrounded by a novel (P, O, C) tridentate ligand resulting from a head-to-head double-insertion of 1-alkyne into the Rh–O

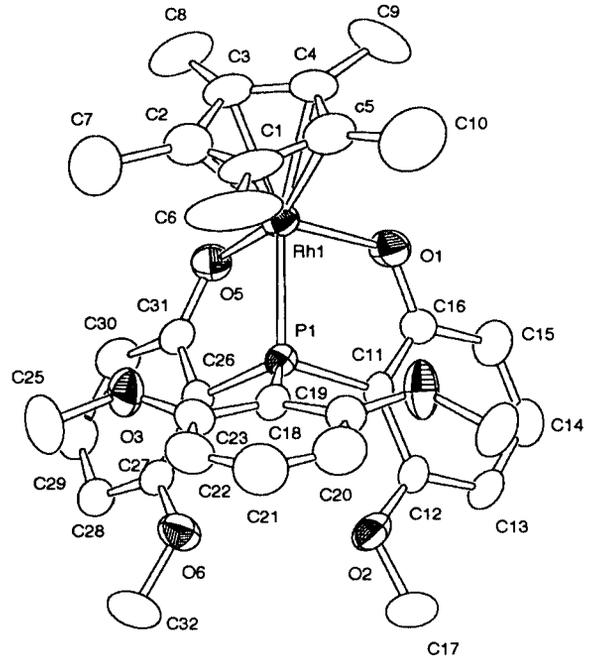


Fig. 2 Molecular structure of **4a**; thermal ellipsoids are drawn to encompass 50% probability.

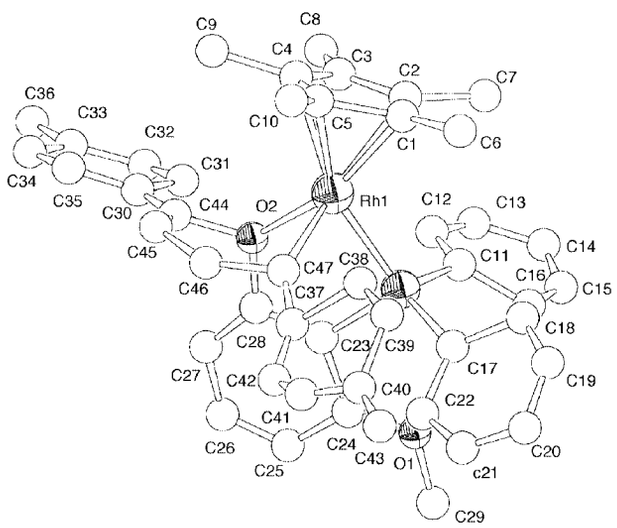


Fig. 3 Molecular structure for the complex cation of **5b**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

bond (Fig. 3). Two carbon atoms bearing a phenyl group are connected to the rhodium and oxygen atoms. The molecule contains five- and six-membered rings through coordination of an ether-O atom. A similar double insertion proceeded on treatment of **1a** with 1-hexyne, giving [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(*O*C(*n*Bu)=CHC(*n*Bu)=*C*H))}](PF_6) **6**; X-ray analysis revealed that the structure consists of a head-to-tail double insertion and a *n*-butyl-substituted carbon atom connected to the O atom (Fig. 4). An olefinic proton in the Rh–CH= moiety appeared at δ 5.69 as a doublet due to coupling with ^{103}Rh. A similar insertion of two PhC≡CH molecules into an Ru–N bond has recently been reported to occur on the triruthenium cluster [Ru_3(μ-H)(μ-N=CPh_2)($CO)_{10}$].[21] An attempt to release the ether O-coordination with xylyl isocyanide was carried out at room temperature for **5a**, however the starting compounds were recovered quantitatively, demonstrating the strength of the ether coordination and the higher stability of five- and six-membered rings.

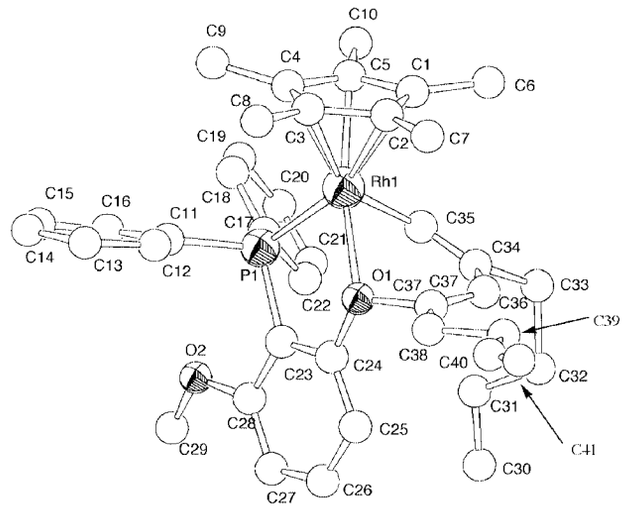


Fig. 4 Molecular structure for the complex cation of **6**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

Complex **1a** in a mixture of acetone and CH_2Cl_2 reacted with HC≡CC_6H_4COOMe-4 bearing an electron-withdrawing substituent at 4-position of the phenyl group in the presence of KPF_6 to give the head-to-head double insertion complex **5c**, [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(*O*C(C_6H_4-4-COOMe)=CHCH=*C*(C_6H_4-4-COOMe))}](PF_6) (Fig. 5) and Cp*$RhCl_2$-[*P*Ph$_2${CH=C(C_6H_4-4-COOMe)(C_6H_3-2-(MeO)-6-(OH))}] **7**.

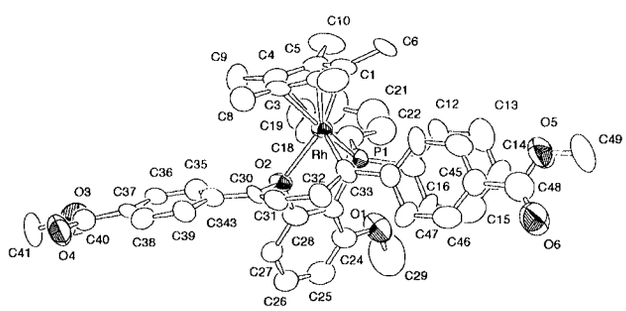
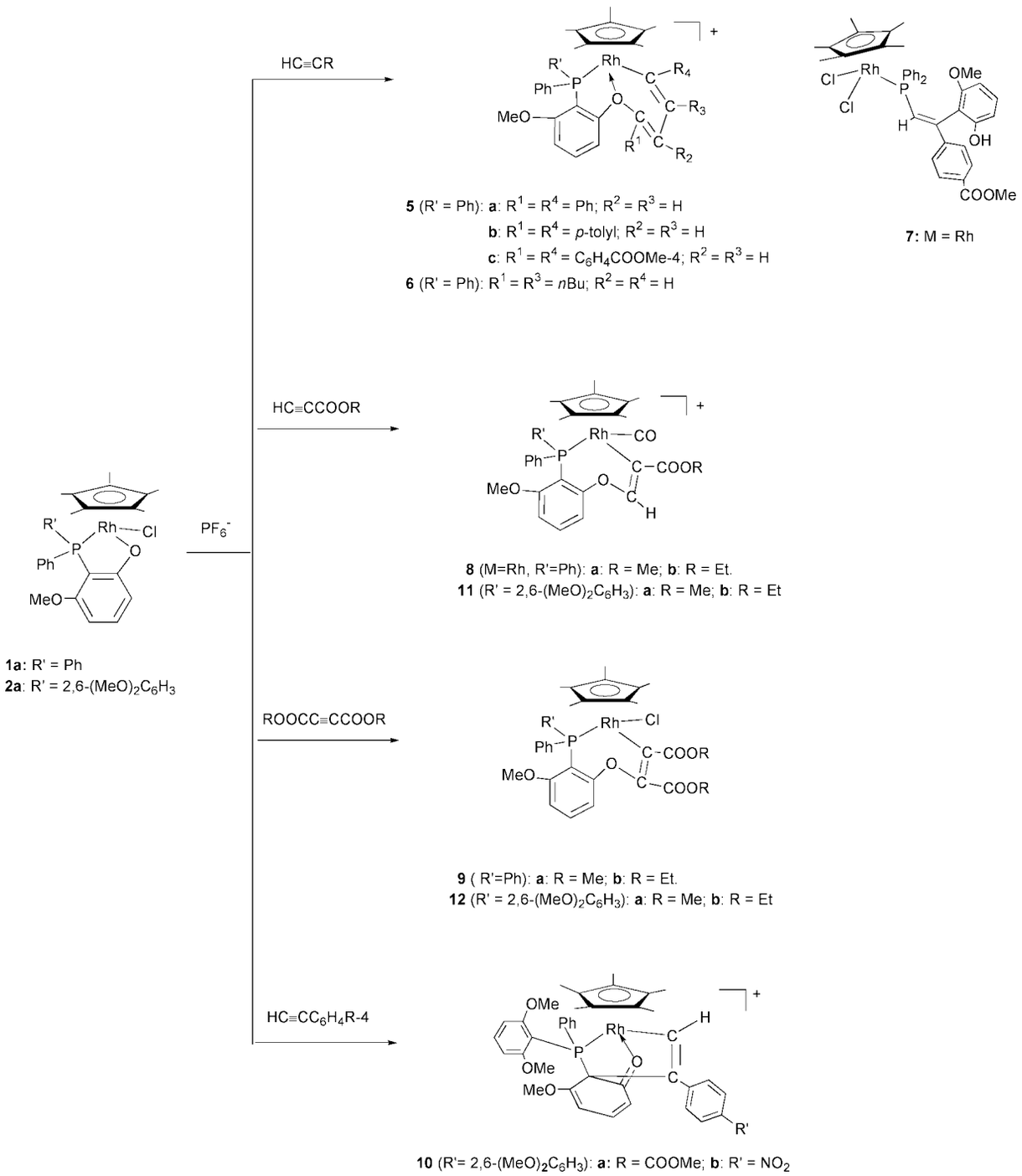


Fig. 5 Molecular structure for the complex cation of **5c**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

The IR spectrum of **7** indicated three characteristic bands at 3285, 1717 and 1605 cm^{-1}, attributable to ν(OH), ν(C=O) and ν(C=C), respectively. The ^{1}H NMR spectrum showed a broad resonance at δ 6.74 due to a hydroxyl proton in addition to three characteristic methyl resonances at δ 1.41 (d), 3.44 (s) and 3.83 (s) due to the presence of pentamethylcyclopentadienyl, methoxy and methoxycarbonyl groups, respectively. The signal at δ 6.74 disappeared by addition of D_2O. There were no signs of a PF_6 group in the IR and ^{31}P{^{1}H} NMR spectra, suggesting that the complex was neutral. The structure was confirmed by X-ray analysis and has been reported in the communication.[19] As expected, the molecule is neutral and the rhodium atom is surrounded by two chlorine atoms and one phosphorus atom. *Cis*-insertion of 1-alkyne into the P–C_{ipso} bond of the phosphine ligand occurred, accompanied by the cleavage of an Rh–O bond. In order to examine the origin of the chlorine atoms, reaction in MeOH was carried out. The fact that the only isolable complex is **5c** indicated that the chlorine atom in **7** originated from dichloromethane.

Complex **1a** reacted readily with an excess of HC≡CCOOMe under similar conditions, giving yellow orange crystals of [Cp*-Rh(CO){*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OCH=*C*(COOMe)))}](PF_6) **8a**. IR bands at 2060 and 1699 cm^{-1} were assigned to terminal CO and carbomethoxy groups, respectively. The presence of



Scheme 2 Reactions of [Cp*RhCl(MDMPP-*P*,*O*)] **1a** and [Cp*RhCl(BDMPP-*P*,*O*)] **2a** with alkynes in the presence of PF_6 anions; PF_6 anions are omitted for clarity.

a PF_6 anion was confirmed by a *ν*(PF) band at 837 cm^{-1} in the IR spectrum and a septet at δ −143.9 in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum exhibited three characteristic bands at δ 1.54 (d), 3.16 (s) and 3.76 (s), assigned to Cp*, methoxy, and carbomethoxy protons, respectively. The $^{31}P\{^1H\}$ NMR spectrum showed a signal at δ 3.12 as a doublet. X-Ray analysis revealed that the Rh atom is surrounded by a CO and a P–C bidentate ligand formed by an insertion of methyl propiolate into the rhodium–oxygen σ-bond (Fig. 6). The carbon atom bearing the carbomethoxy group occupied a rhodium site regioselectively as a result of the polarity of the Rh–O and C≡C bonds. A similar complex **8b** was obtained by reaction with HC≡CCOOEt. In order to examine the origin of the carbonyl ligand, the reaction was carried out in THF and gave **8a** in high yield, suggesting that the CO group originates from propiolate. Abstraction of CO from the ester groups is quite rare, although $Ni(CO)(PPh_3)_3$ [22] from the reaction of $Ni(cod)_2$ with triphenylphosphine and phenyl propionate, and $Rh(OAr)(CO)L_2$ [23] from MeCOOAr and $RhHL_4$ (L = phosphine), have been documented.

Reactions with internal alkynes such as MeC≡CPh and ROOCC≡CCOOR (R = Me, Et) were carried out in the presence of $NaPF_6$. The former failed to react, whereas the latter produced reddish orange complexes (**9a**: R = Me; **9b**: R = Et) formulated as [Cp*RhCl{$PPh_2(C_6H_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}]. Mass spectrometry revealed the masses of **9a** and **9b** to be *m*/*z* 709 and 737, respectively, calculated on the basis of the loss of a CO molecule from the molecular peaks. The IR spectrum of **9b** showed two bands at 1705 and 1589 cm^{-1} for a carbonyl group and a C–C double bond, respectively. However, there were no bands at *ca.* 840 cm^{-1} attributable to the PF_6 group. In the ^1H NMR spectrum, two methylene protons of two COOEt groups gave rise to multiplets at δ 4.03 and 4.18. Each multiplet was observed as a

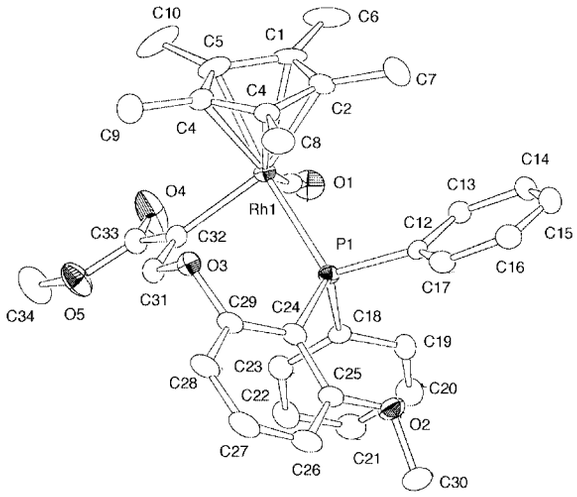


Fig. 6 Molecular structure for the complex cation of **8a**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

result of inequivalence of methylene protons CH_aH_b arising from a chiral center of the Rh metal. The methyl protons appeared at δ 1.03 and 1.27 as triplets seemingly, due to same coupling constants ($J_{HHa} = J_{HHb}$) with each methylene proton, H_a and H_b.

The spectroscopic data suggested that the complex is a seven-membered metallacycle derived from the insertion of EtOOCC≡CCOOEt. The proposed structure was confirmed by X-ray analysis.[19] When this reaction was performed without PF_6^- ions, the starting materials were recovered quantitatively. A similar reaction in the presence of $NaClO_4$ gave **9a**, whereas that in the presence of [nBu$_4$N]Cl failed to react, suggesting that the presence of large anions such as PF_6^- and ClO_4^- is indispensable for this reaction and an initial extraction of Cl anion is a driving force.

Reactions of [Cp*RhCl(BDMPP-*P*,*O*)] 2a with alkynes

Reactions of **2a** containing the bidentate bulky phosphine ligand BDMPP-*P*,*O* with ethynylbenzene or 1-hexyne failed to give isolable complexes. When **2a** in a mixture of CH_2Cl_2 and acetone was treated with 1-ethynylbenzene derivatives bearing an electron-withdrawing substituent such as COOMe or NO_2 in the presence of KPF_6 at room temperature, complexes **10** with empirical formulae [Cp*Rh(BDMPP-*P*,*O*)(HC≡CC$_6$H$_4$R-4)](PF$_6$) (**a**: R = COOMe, **b**: R = NO_2) as determined from elemental analyses and FAB mass spectroscopy were generated.

It was confirmed by X-ray analysis of **10b** that the structure contains five- and six-membered rings derived from an unprecedented transannular addition of 1-alkyne between the Rh atom and the *ipso*-carbon atom of the phosphine ligand, and subsequent transformation of the O donor from a phenoxide to an ether coordination (Fig. 7). The IR spectra showed bands at 1715 and 1630 cm^{-1} due to methoxycarbonyl and ketone groups, respectively, for **10a**, and at 1628 cm^{-1} due to a ketone group for **10b**. The ^{1}H NMR spectra showed three methoxy groups at δ *ca.* 3.0(s), 3.1(bs) and 3.5(bs) for **10a** and **10b**, and a further peak due to a methoxycarbonyl group at δ 3.84(s) for **10a**. A remarkable feature is that the ^{31}P{^{1}H} NMR doublets showed large downfield shifts (δ *ca.* 140).

Reactions of **2a** with HC≡CCOOR (R = Me, Et) in the presence of KPF_6 at room temperature led to an insertion of 1-alkyne into the Rh–O σ-bond to give the seven-membered complexes [Cp*Rh(CO){*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OCH=*C*(COOR)))}](PF$_6$) **11** (**a**: R = Me; **b**: R = Et). The IR spectra showed two characteristic bands at *ca.* 2060 and 1690 cm^{-1} due to terminal CO and methoxycarbonyl groups, respectively. The ^{1}H NMR spectra showed the presence of three

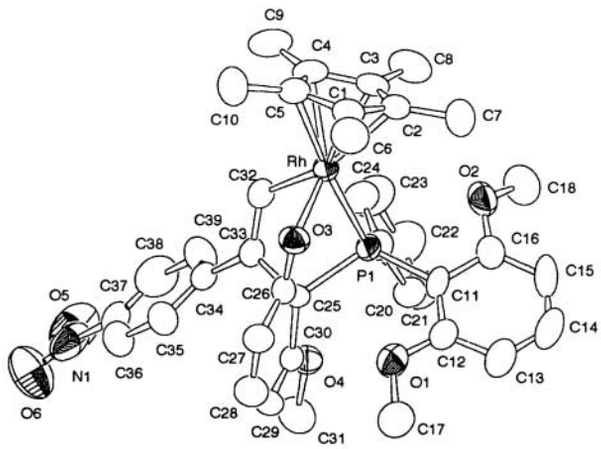


Fig. 7 Molecular structure for the complex cation of **10b**·3H$_2$O; the PF_6 cation and H_2O molecules were omitted for clarity and thermal ellipsoids are drawn to encompass 30% probability.

methoxy groups. X-Ray analysis of **11a** revealed that the molecule contains a CO group and a (P,C) bidentate ligand resulting from a regioselective insertion of 1-alkyne into the Rh–O bond (Fig. 8). The carbon atom bearing the carbomethoxy group is connected to the Rh atom as well as that in **8**. The ^{31}P{^{1}H} NMR doublets appeared at δ *ca.* −13, at higher fields than those (δ *ca.* 3.2) for **8**.

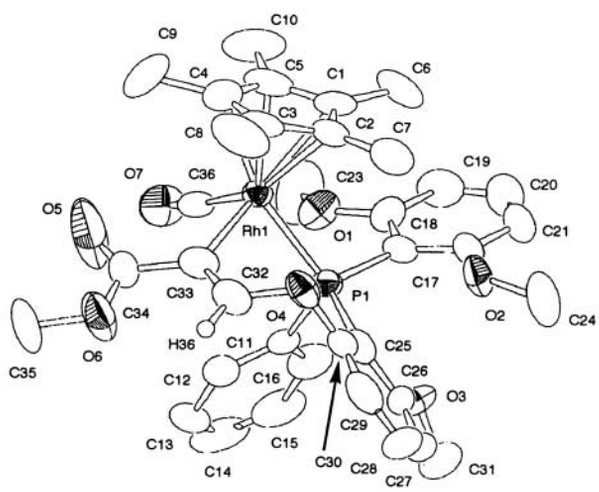
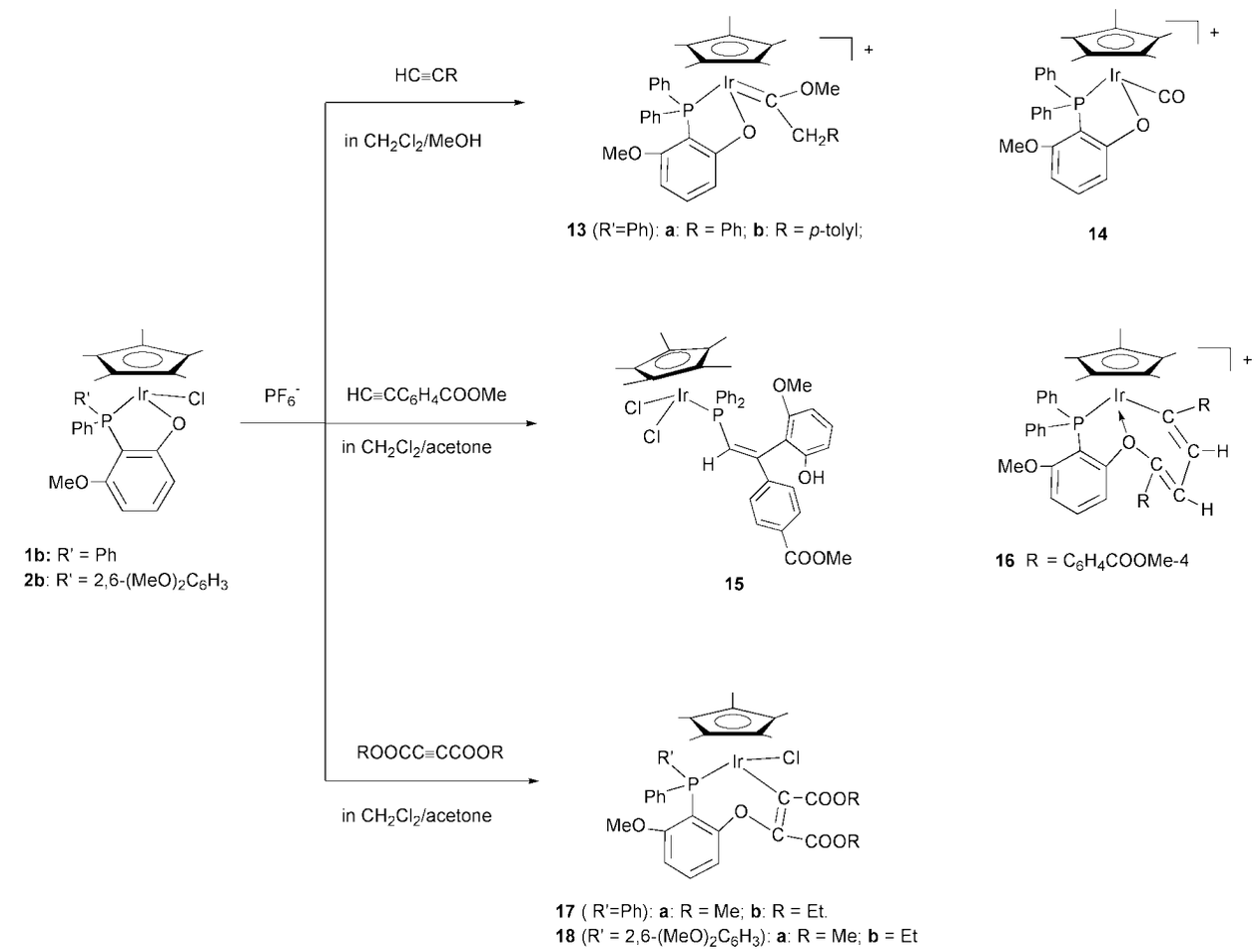


Fig. 8 Molecular structure for the complex cation of **11a**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

Acetylene dicarboxylate was treated with **2a** in the presence of KPF_6 at room temperature, leading to an insertion into the Rh–O bond and yielding reddish orange complexes, [Cp*-RhCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}] (**12a**: R = Me; **12b**: R = Et) (Fig. 9). The IR spectra showed a band at *ca.* 1705 cm^{-1} due to the C–O double bond. The chemical shift of the coordinated P atom in the ^{31}P{^{1}H} NMR spectra appeared at δ *ca.* −2.0 as doublets appearing at higher fields than those (δ *ca.* 10) for **9**.

Reactions of [Cp*IrCl(MDMPP-*P*,*O*)] 1b or [Cp*IrCl-(BDMPP-*P*,*O*)] 2b with alkynes

Overall reactions for iridium complexes are depicted in Scheme 3. Reaction of **1b** with HC≡CR (R = Ph, *p*-Tolyl) in a mixture of CH_2Cl_2 and MeOH was carried out in the presence of KPF_6, giving the carbene complexes **13**, [Cp*Ir(MDMPP-*P*,*O*){=C(OMe)CH$_2$R}](PF$_6$) (**a**: R = Ph; **b**: R = *p*-Tolyl) as main products and carbonyl complex **14** [Cp*Ir(MDMPP-*P*,*O*)(CO)](PF$_6$) as a by-product, unlike the rhodium complexes. Complex **14** was confirmed as a product derived from



Scheme 3 Reactions of [Cp*IrCl(MDMPP-*P*,*O*)] **1b** and [Cp*IrCl(BDMPP-*P*,*O*)] **2b** with alkynes in the presence of PF_6 anions; PF_6 anions are omitted for clarity.

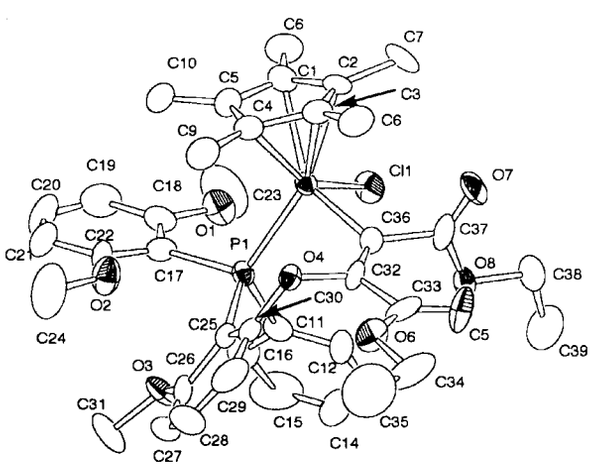


Fig. 9 Molecular structure for the complex cation of **12b**; thermal ellipsoids are drawn to encompass 50% probability.

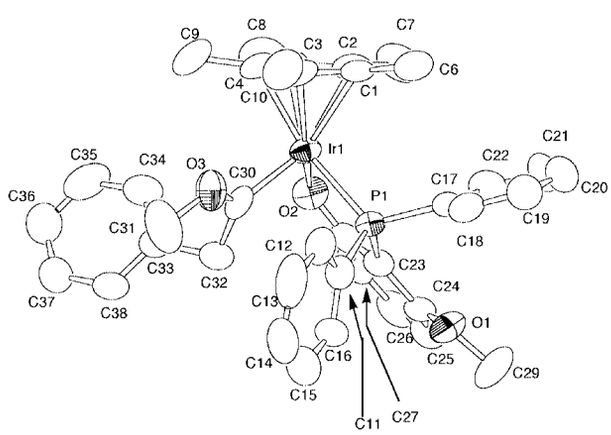


Fig. 10 Molecular structure for the complex cation of **13a**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

water in MeOH.[24] Carbene structures were confirmed by X-ray analysis of **13a** (Fig. 10).

Reaction of **1b** with HC≡CC$_6$H$_4$COOMe-4 proceeded in a similar way to the rhodium analog, forming two complexes; a P–C insertion product **15** Cp*IrCl$_2$[*P*Ph$_2${CH=C(C$_6$H$_4$-4-COOMe)(C$_6$H$_3$-2-(MeO)-6-(OH))}] and a head-to-head double insertion product **16** [Cp*Ir{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*C(C$_6$H$_4$-4-COOMe)=CHCH=*C*(C$_6$H$_4$-4-COOMe)))}](PF$_6$). The IR spectrum of **15** showed two characteristic bands at 3312 and 1717 cm^{-1}, due to the OH and C–O double bonds. The ^{1}H NMR spectrum showed four resonances at δ 1.44 (d), 3.45 (s), 3.84 (s) and 6.64(bs) due to Cp*, MeO, COOMe and OH protons, respectively. The IR spectrum of **16** showed bands at 1721 and 843 cm^{-1} for ν(C=O) and ν(PF$_6$) groups, respectively. The ^{1}H NMR spectrum showed resonances at δ 3.67 due to a methoxy group and at δ 3.89 and 3.90 due to two methoxycarbonyl groups.

Complex **1b** reacted readily with ROOCC≡CCOOR (R = Me, Et) in the presence of KPF_6 to produce insertion products **17**, [Cp*IrCl{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}] (**a**: R = Me; **b**: R = Et). A similar insertion reaction occurred for **2b**, giving **18** [Cp*IrCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))}] (**a**: R = Me; **b**: R = Et). The IR spectra of **17** and **18** showed a band at *ca.* 1700 cm^{-1} due to ν(CO). In the ^{1}H NMR spectra the methoxy protons appeared at δ *ca.* 3.2 for **17** and at δ *ca.* 3.0, 3.2 and 3.6 for **18**, showing the

NMR patterns similar to the rhodium analogs (**9** and **12**). In the $^{31}P\{^{1}H\}$ NMR spectra the chemical shift values (δ *ca.* −24) of the coordinated P atoms in **17** showed downfield shifts compared to those (δ *ca.* −36) of **18**. A similar trend has been observed in rhodium complexes **9** and **12** (*vide supra*). Finally the detailed structures were confirmed by X-ray analyses of **18a** and **18b** (Fig. 11 and 12).

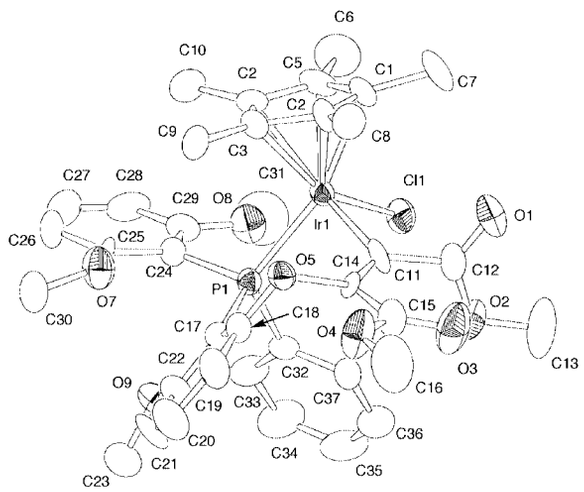


Fig. 11 Molecular structure for the complex cation of **18a**; thermal ellipsoids are drawn to encompass 50% probability.

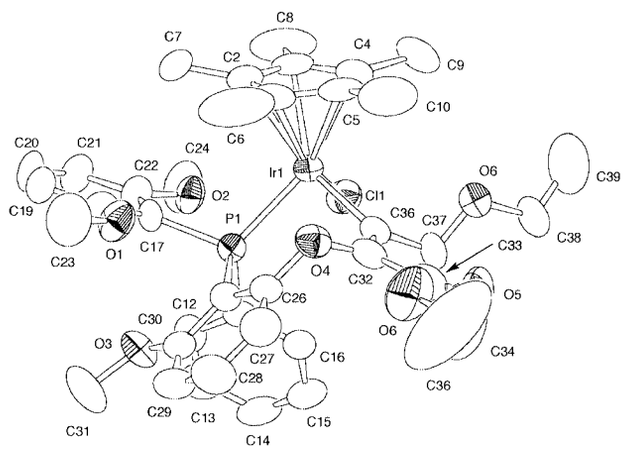


Fig. 12 Molecular structure for the complex cation of **18b**; thermal ellipsoids are drawn to encompass 50% probability.

Reactions of 9 and 14

When complex **9** was treated with xylyl (Xyl) or mesityl (Mes) isocyanide in the presence of KPF_6 or Ag(OTf), a substitution reaction occurred readily to produce **19** [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OC(COOR)=*C*(COOR))}](CNR′)]X (R = Me (**a**), Et (**b**); R′ = Xyl (**c**), Mes (**d**); X = PF_6 (**e**), OTf (**f**)) (Scheme 4). The IR spectra showed bands at *ca.* 2160 and 1720 cm^{-1} attributable to isocyanide and carboalkoxy groups, respectively. The ^{1}H NMR spectra of [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-{OC(COOMe)=*C*(COOMe))}(CNR′)]X, **19ace** (R′ = Xyl; X = PF_6), **19acf** (R′ = Xyl; X = OTf) and **19adf** (R′ = Mes; X = OTf), showed two singlets at δ *ca.* 3.8 due to the methoxycarbonyl groups. Those of [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OC(COOEt)=*C*(COOEt)))}(CNR′)](OTf), **19bcf** (R′ = Xyl) and **19bdf** (R′ = Mes), showed two triplets at δ *ca.* 1.3 due to the methyl groups of esters. Methylene protons appeared at δ *ca.* 4.2 as a quartet, probably due to accidental degeneracy of chemical shifts. The $^{31}P\{^{1}H\}$ NMR spectra showed a doublet at δ *ca.* 7.0. It was confirmed by X-ray analysis of **19bcf** that the rhodium atom was surrounded by one P and two C atoms (Fig. 13). A similar reaction of **9a** with carbon monoxide was

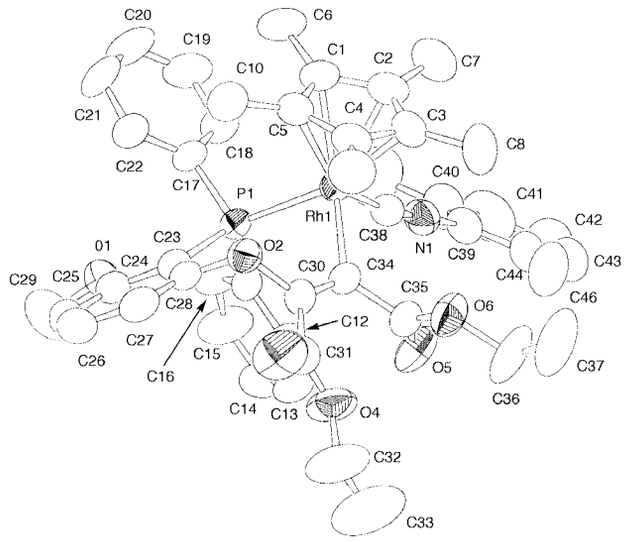


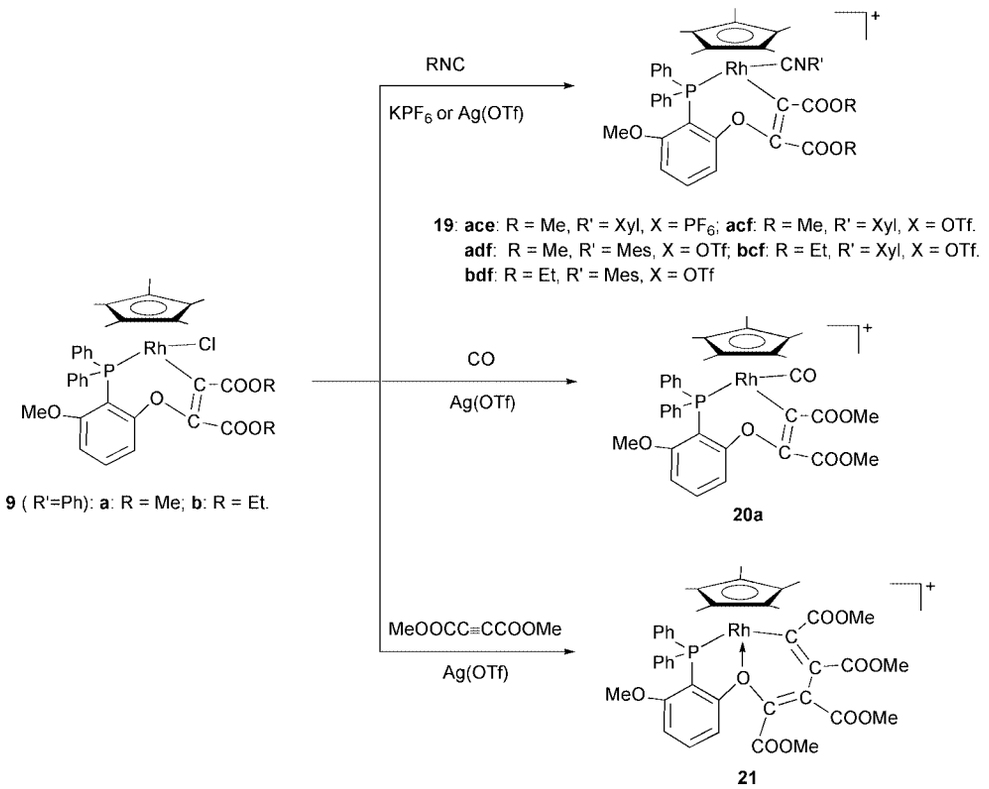
Fig. 13 Molecular structure for the complex cation of **19bcf**; the PF_6 cation was omitted for clarity and thermal ellipsoids are drawn to encompass 50% probability.

carried out in the presence of Ag(OTf) to generate [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OC(COOMe)=*C*(COOMe)))}(CO)](OTf) **20a** in high yield (Scheme 4). The IR spectrum showed bands at 2068 cm^{-1} for a CO ligand and 1715 cm^{-1} for the carbonyl groups.

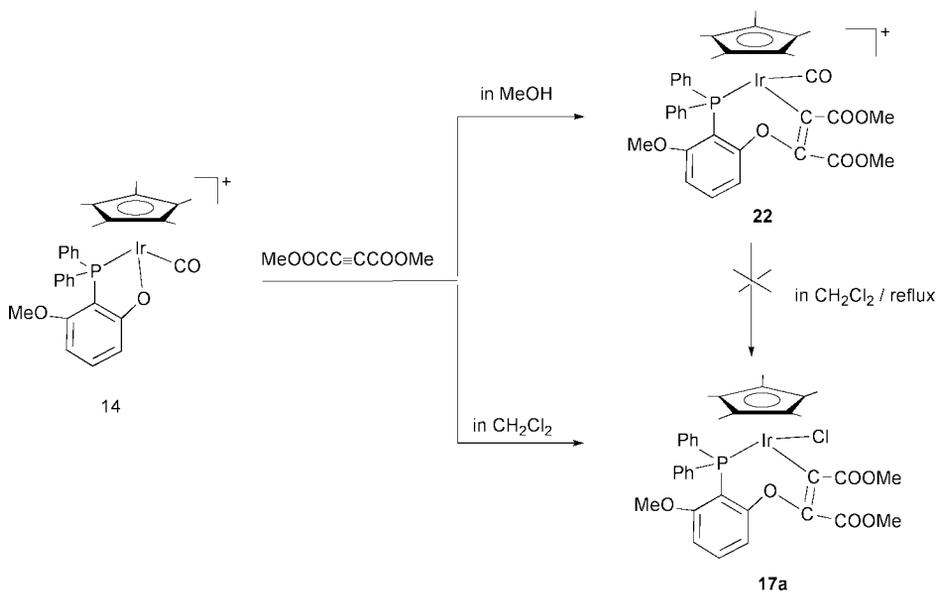
In an attempt to examine coordination ability between ligands, the substitution reactions of **19** or **20a** with another ligand were carried out. Carbonyl complex **20a** reacted readily with 10 equiv. of isocyanide to form corresponding isocyanide complexes **19acf** and **19adf** quantitatively, however, isocyanide complexes failed to react with CO. The coordination ability of isocyanide is stronger than that of CO. No ligand exchange between the isocyanide complex and another isocyanide was observed spectroscopically.

When **9a** and MeOOCC≡CCOOMe was treated with Ag(OTf) in a mixture of MeOH and CH_2Cl_2, orange crystals **21** with an empirical formula of [Cp*Rh(MDMPP-*P*,*O*)-(MeOOCC≡CCOOMe)$_2$](OTf) from the elemental analysis was generated. Mass spectrometry revealed the mass to be *m*/*z* 828 ($[M - 1]^+$) (M = a cationic part). The IR spectrum showed ν(C=O) bands at 1732 and 1709 cm^{-1}. In the ^{1}H NMR spectrum, six methyl protons consisting of a doublet and five sharp singlets appeared at δ 1.48 (d), 2.79, 3.44, 3.55, 3.92 and 4.05, showing that two resonances at δ 1.48 (d) and 2.79 are assignable to Cp* and methoxy protons, respectively. Other resonances are due to carbomethoxy protons, suggesting the presence of four kinds of methoxycarbonyl groups. The $^{31}P\{^{1}H\}$ NMR spectrum showed a doublet at δ 35.3 (J_{RhP} = 148 Hz). From these spectroscopic data, the complex is assumed to be a double insertion product of acetylene dicarboxylate into the Rh–C bond (Scheme 4). Analogously, complex **21** was generated directly from the reaction of **1a** with MeOOCC≡CCOOMe in the presence of Ag(OTf).

Reaction of **14** with MeOOCC≡CCOOMe in a mixture of MeOH and CH_2Cl_2 at reflux, led to an insertion of alkyne into the Ir–O bond to give **17a** and [Cp*Ir(CO){*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OC(COOMe)=*C*(COOMe)))}](PF$_6$) **22**. In order to examine the origin of the Cl atom, the reactions in MeOH or CH_2Cl_2 were carried out. The former gave **22** and the latter gave **17a** exclusively, showing that origin of the Cl atom was derived from dichloromethane (Scheme 5). When **22** was refluxed in CH_2Cl_2, the starting complex was recovered quantitatively. These results suggest that the route **14** ⟶ **22** ⟶ **17a** can be ruled out for the formation of **17a**. Complex **17a** was formed by an initial formation of **1b** arising from an extraction of chlorine anion from CH_2Cl_2 and a subsequent insertion of MeOOCC≡



Scheme 4 Reactions of **9** with Lewis bases or MeOOCC≡CCOOMe; PF_6 or TfO anions are omitted for clarity.



Scheme 5 Reactions of [Cp*Ir(CO)(MDMPP-*P*,*O*)](PF$_6$) with MeOOCC≡CCOOMe in MeOH or CH_2Cl_2; PF_6 anions are omitted for clarity.

CCOOMe into the Ir–O bond of **1b**. Complex **22** was formed directly by an insertion of alkyne into the Ir–O bond of **14**.

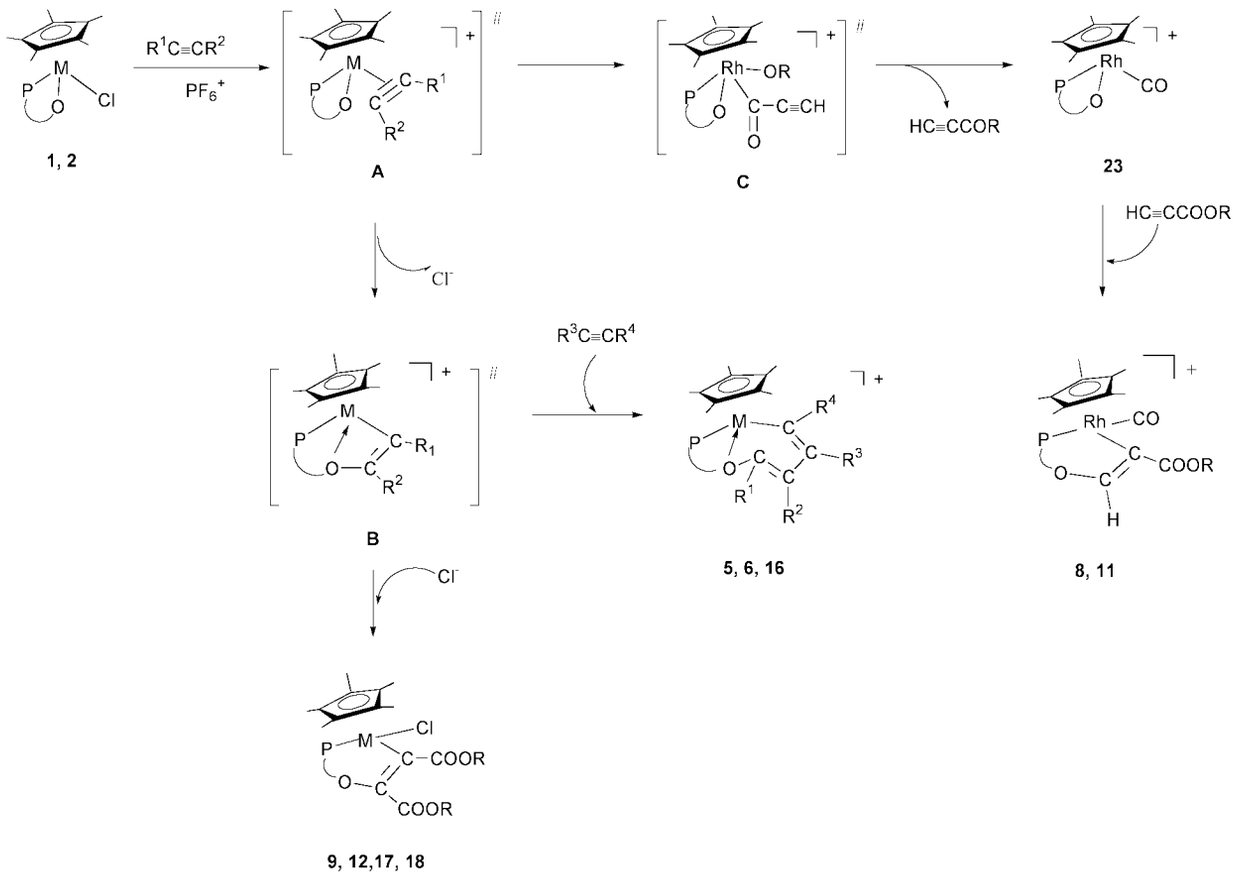
Pathways for the formation of insertion complexes

A possible route for the insertion of alkyne into the metal–oxygen bond is depicted in Scheme 6. Initially, the reaction consists of the usual substitution of alkyne to form an intermediate **A**. An insertion of alkyne into the metal–oxygen bond gives an intermediate **B**, and a nucleophilic attack of a Cl anion on the intermediate **B** produces **9**, **12**, **17** or **18**. The double-insertion products (**5**, **6** or **16**) are generated by the regio-selective insertion of a second alkyne into the metal-carbon bond of the intermediate **B**.

An intermediate **C** is formed by an oxidative addition of ester to the rhodium metal, accompanied by an elimination of HC≡COR, giving the carbonyl complex **23**, [Cp*Rh(CO)-{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-*O*)}](PF$_6$). Finally, complex **8** or **11** is formed by the insertion of propiolate into the Rh–O bond of the carbonyl complex. The final process was confirmed by the facts that **23** prepared independently[12] reacted readily with HC≡CCOOMe to give **8a** and the reaction of the iridium complex **14** with MeOOCC≡CCOOMe in MeOH gave the insertion product **22** (Scheme 5). The formation of HC≡COEt and **8b** was confirmed by monitoring the reaction of **1a** and HC≡CCOOEt by means of NMR spectroscopy. As yet, no intermediate **B** has been isolated because of the instability of the four-membered ring structure.

Molecular structures

Since perspective drawings, selected bond lengths and angles of **5a**, **7**, and **9b** have already been reported in the literature,[19,20]



Scheme 6 Possible pathway for the insertion reaction of alkynes (PO = PPh$_2$(C$_6$H$_3$-6-(MeO)-2-O) or PPh{C$_6$H$_3$-2,6-(MeO)$_2$}{C$_6$H$_3$-6-(MeO)-2-O}.

Table 1 Selected bond lengths (Å) and angles (°) for [Cp*RhCl(BDMPP-P,O)] **2a** and [Cp*Rh (TDMPP-P,O,O')] **4a**

2a					
Rh(1)–P(1)	2.323(2)	Rh(1)–O(2)	2.050(5)	Rh(1)–Cl(2)	2.390(2)
O(2)–C(16)	1.302(8)	C(11)–C(16)	1.41(1)	P(1)–C(11)	1.811(7)
P(1)–Rh(1)–O(2)	83.0(1)	P(1)–Rh(1)–Cl(1)	87.30(7)	O(2)–Rh(1)–Cl(1)	89.5(2)
Rh(1)–O(2)–C(16)	120.7(5)	O(2)–C(16)–C(11)	123.1(6)	P(1)–C(11)–C(16)	113.7(5)
Rh(1)–P(1)–C(11)	99.4(3)				
4a					
Rh(1)–P(1)	2.274(2)	Rh(1)–O(1)	2.065(5)	Rh(1)–O(5)	2.068(5)
O(1)–C(16)	1.334(8)	C(11)–C(16)	1.395(9)	P(1)–C(11)	1.811(7)
O(5)–C(31)	1.306(8)	C(26)–C(31)	1.414(9)	P(1)–C(26)	1.809(6)
P(1)–Rh(1)–O(1)	83.3(1)	P(1)–Rh(1)–O(5)	80.9(1)	O(1)–Rh(1)–O(5)	88.0(2)
Rh(1)–O(1)–C(16)	119.4(4)	O(1)–C(16)–C(11)	121.8(6)	P(1)–C(11)–C(16)	114.6(5)
Rh(1)–P(1)–C(11)	100.6(2)	Rh(1)–O(5)–C(31)	120.7(4)	O(5)–C(31)–C(26)	121.5(6)
P(1)–C(26)–C(31)	111.7(5)	Rh(1)–P(1)–C(26)	101.2(2)		

their structures were omitted here. However, the structure of **10b** is discussed because of brief description in literature.[20]

Crystal structures of 2a and 4a. Perspective drawings of **2a** and **4a** with atomic numbering schemes are given in Figs. 1 and 2, respectively, and selected bond lengths and angles are listed in Table 1. The molecule of **2a** has two chiral centers (Rh and P atoms). The priority order of the ligands is Cp* > Cl > P > O for a metal center and Rh > 2-O-6-(MeO)C$_6$H$_3$ > 2,6-(MeO)$_2$C$_6$H$_3$ > Ph for a P atom. Fig. 1 shows that the molecule is a Rh$_R$P$_R$/Rh$_S$P$_S$ pair. Complex **4a** has a (P,O,O′) tridentate ligand constructed by two five-membered rings. The Rh–P bond length of 2.323(2) Å for **2a** is longer by 0.05 Å than that for **4a**. The P–Rh–O bite angles of both complexes are *ca.* 82°, comparing well with those of iridium and ruthenium complexes.[10–12]

Structures of 5b, 5c and 6. Perspective drawings of **5b**, **5c** and **6** with atomic numbering schemes are given in Fig. 3–5, and selected bond lengths and angles are listed in Tables 2 and 3. All complexes consist of two metallacycles derived from a double insertion of alkyne and a transformation of the O donor from a phenoxide to an ester coordination, and all are constructed from five- and six-membered rings shared by a Rh atom, derived in **5** from a head-to-head double insertion of the alkyne and in **6** from a head-to-tail double insertion product. The Rh–P bond lengths of **5** and **6** are in the range 2.268–2.300 Å, similar to that of **1a**,[12] whereas the average Rh–O coordination bond length is 2.218 Å, being *ca.* 0.15 Å longer than that of **1a**, as expected for ether coordination as opposed to a phenoxide. The P–Rh–O bite angles of the five-membered ring were 80°, and the O–Rh–C bite angles of the six-membered ring are in the range 80–81°. These bite angles are independent of the ring size. The P–Rh–C bond angles are wider by *ca.* 10° than those of five- and six-membered rings. The average length of two double bonds in the metallacyclohexadiene rings is *ca.* 1.33 Å, being usual C–C double bonds.

Table 2 Selected bond lengths (Å) and angles (°) for [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(*O*C(Tolyl)=CHCH=*C*(Tolyl)))}](PF$_6$) **5b** and [Cp*Rh{PPh$_2$(C_6H_3-2-(MeO)-6-(OC(C_6H_4-4-COOMe)=CHCH=*C*(C_6H_4-4-COOMe)))}](PF$_6$) **5c**

5b					
Rh(1)–P(1)	2.30(1)	Rh(1)–O(2)	2.21(2)	Rh(1)–C(47)	2.14(4)
O(2)–C(44)	1.49(4)	C(44)–C(45)	1.35(4)	C(45)–C(46)	1.41(4)
C(46)–C(47)	1.38(5)	P(1)–C(23)	1.87(4)	C(23)–C(28)	1.38(4)
O(2)–C(28)	1.36(4)				
P(1)–Rh(1)–O(2)	80.0(7)	P(1)–Rh(1)–C(47)	91(1)	O(2)–Rh(1)–C(47)	81(1)
Rh(1)–O(2)–C(28)	121(2)	O(2)–C(28)–C(23)	115(3)	P(1)–C(23)–C(28)	118(3)
Rh(1)–P(1)–C(23)	100(1)	Rh(1)–O(2)–C(44)	115(1)	O(2)–C(44)–C(30)	115(3)
O(2)–C(44)–C(45)	108(3)	Rh(1)–C(47)–C(37)	129(3)	Rh(1)–C(47)–C(46)	111(3)
C(37)–C(47)–C(46)	119(4)	C(28)–O(2)–C(44)	111(2)		
5c					
Rh(1)–P(1)	2.300(3)	Rh(1)–O(2)	2.214(7)	Rh(1)–C(33)	2.06(1)
O(2)–C(30)	1.43(1)	C(30)–C(31)	1.33(2)	C(31)–C(32)	1.45(2)
C(32)–C(33)	1.33(2)	P(1)–C(23)	1.81(1)	C(23)–C(28)	1.37(2)
O(2)–C(28)	1.44(1)				
P(1)–Rh(1)–O(2)	80.2(2)	P(1)–Rh(1)–C(33)	91.1(3)	O(2)–Rh(1)–C(33)	80.8(4)
Rh(1)–O(2)–C(28)	119.3(7)	O(2)–C(28)–C(23)	116.1(10)	P(1)–C(23)–C(28)	119.4(9)
Rh(1)–P(1)–C(23)	102.7(4)	Rh(1)–O(2)–C(28)	119.3(7)	O(2)–C(30)–C(31)	115(1)
C(30)–C(31)–C(32)	125(1)	C(31)–C(32)–C(33)	128(1)	Rh(1)–C(33)–C(32)	118(1)

Table 3 Selected bond lengths (Å) and angles (°) for [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(MeO)-6-(*O*C(*n*Bu)CH=C(*n*Bu)=*C*H))}](PF$_6$) **6**

Rh(1)–P(1)	2.268(5)	Rh(1)–O(1)	2.23(1)	Rh(1)–C(35)	2.01(2)
O(1)–C(37)	1.46(2)	C(36)–C(37)	1.33(2)	C(34)–C(36)	1.49(3)
C(34)–C(35)	1.30(2)	P(1)–C(23)	1.82(2)	C(23)–C(24)	1.34(2)
O(1)–C(24)	1.45(2)				
P(1)–Rh(1)–O(1)	80.3(3)	P(1)–Rh(1)–C(35)	88.1(6)	O(1)–Rh(1)–C(35)	80.0(6)
Rh(1)–O(1)–C(24)	116.0(10)	Rh(1)–O(1)–C(37)	108.9(10)	C(24)–O(1)–C(37)	117(1)
O(1)–C(24)–C(23)	118(1)	P(1)–C(23)–C(24)	117(1)	Rh(1)–P(1)–C(23)	103.5(6)
O(1)–C(37)–C(36)	115(1)	O(1)–C(37)–C(38)	111(1)	C(34)–C(36)–C(37)	125(1)
C(36)–C(34)–C(35)	122(1)	C(33)–C(34)–C(36)	114(1)	Rh(1)–C(35)–C(34)	124(1)

Table 4 Selected bond lengths (Å) and angles (°) for [Cp*Rh(CO){*P*Ph$_2$(C_6H_3-2-(MeO)-6-(OCH=*C*(COOMe)))}](PF$_6$) **8a** and [Cp*Rh(CO)-{*P*Ph(C_6H_3-2,6-(MeO)$_2$)(C_6H_3-2-(MeO)-6-(OCH=*C*(COOMe)))}](PF$_6$)(PF$_6$) **11a**

8a					
Rh(1)–P(1)	2.349(1)	Rh(1)–C(11)	1.909(6)	Rh(1)–C(32)	2.072(5)
C(11)–O(1)	1.128(6)	C(31)–C(32)	1.309(8)	O(3)–C(31)	1.412(6)
C(24)–C(29)	1.391(8)	P(1)–C(24)	1.816(5)	C(32)–C(33)	1.487(7)
O(4)–C(33)	1.199(7)	O(5)–C(33)	1.337(7)		
P(1)–Rh(1)–C(11)	89.6(2)	P(1)–Rh(1)–C(32)	86.5(1)	C(11)–Rh(1)–C(32)	93.2(2)
Rh(1)–P(1)–C(24)	118.8(2)	P(1)–C(24)–C(29)	123.0(4)	O(3)–C(29)–C(24)	119.9(5)
O(3)–C(31)–C(32)	119.7(5)	Rh(1)–C(32)–C(31)	120.0(4)	Rh(1)–C(11)–O(1)	173.5(5)
11a					
Rh(1)–P(1)	2.364(6)	Rh(1)–C(33)	2.15(2)	Rh(1)–C(36)	2.05(3)
C(36)–O(7)	1.04(3)	C(32)–C(33)	1.32(3)	O(4)–C(32)	1.44(3)
O(4)–C(30)	1.40(3)	P(1)–C(25)	1.89(2)	C(25)–C(30)	1.40(3)
O(5)–C(34)	1.14(3)	O(6)–C(34)	1.29(3)		
P(1)–Rh(1)–C(33)	89.7(7)	P(1)–Rh(1)–C(36)	90.8(7)	C(33)–Rh(1)–C(36)	89.8(10)
Rh(1)–P(1)–C(25)	118.9(9)	P(1)–C(25)–C(30)	120(1)	C(25)–C(30)–O(4)	121(2)
O(4)–C(32)–C(33)	122(2)	Rh(1)–C(33)–C(32)	116(2)	Rh(1)–C(33)–C(34)	122(1)
Rh(1)–C(36)–O(7)	175(2)				

Structures of 8a and 11a. Perspective drawings of **8a** and **11a** with atomic numbering schemes are given in Figs. 6 and 8, respectively, and selected bond lengths and angles are listed in Table 4. The Rh atom is surrounded by a CO ligand and a P–O bidentate ligand derived from the insertion of propiolate into the Rh–O bond. A carbon atom bearing a carbomethoxy group occupies a rhodium site as the result of the polarity of the alkyne. Complex **11a** has two chiral centers. The priority order of the ligands is Cp* > P > CO > C for a Rh center and Rh > 2-O-6-MeOC_6H_3 > 2,6-(MeO)$_2C_6H_3$ > Ph for a P center. Fig. 8 shows a Rh_RP_R/Rh_SP_S pair. The seven-membered rings of **8a** and **11a** are divided into two planes; Rh(1)O(3)C(31)C(32) and Rh(1)P(1)O(3)C(24)C(29) for **8a**, and Rh(1)O(4)C(32)C(33) and Rh(1)P(1)O(4)C(25)C(30) for **11a**; the dihedral angle of the former is 74.6(2)° and that of the latter is 69.7(5)°. The smaller angle of **11a** provides a larger space for the 2,6-(MeO)$_2C_6H_3$ ring. The Rh–P, Rh–*C*(=CH–) and Rh–*C*O bond lengths of **11a** are longer than those of **8a**, mininizing steric repulsion between bulky 2,6-dimethoxyphenyl and pentamethylcyclopentadienyl moieties. The C=C double bond lengths are usual. The Rh–C–O bond angles are the usual value of 174°. The angles around the Rh atom containing the P atom in **11a** are wider than those of **8a**, due to the bulkiness of the 2,6-(MeO)$_2C_6H_3$ (Å) group.

Structures of 12b, 18a and 18b. Perspective drawings of **12b** **18a** and **18b** with atomic numbering schemes are given in Figs. 9, 11 and 12, respectively. Selected bond lengths and angles are listed in Table 5. The molecule is neutral and consists of a

Table 5 Selected bond lengths (Å) and angles (°) for [Cp*RhCl{*P*Ph(C_6H_3-2,6-$(MeO)_2$)(C_6H_3-2-(MeO)-6-(OC(COOR)=*C*(COOR)))] **12b**, [Cp*IrCl{*P*Ph(C_6H_3-2,6-$(MeO)_2$)(C_6H_3-2-(MeO)-6-(OC(COOMe)=*C*(COOMe)))] **18a** and [Cp*IrCl{*P*Ph(C_6H_3-2,6-$(MeO)_2$)(C_6H_3-2-(MeO)-6-(OC(COOEt)=*C*(COOEt)))] **18b**

12b

Rh(1)–P(1)	2.344(3)	Rh(1)–Cl(1)	2.402(3)	Rh(1)–C(36)	2.02(1)
C(32)–C(36)	1.35(2)	O(4)–C(32)	1.39(1)	O(4)–C(30)	1.39(1)
C(25)–C(30)	1.40(1)	P(1)–C(25)	1.86(1)	C(32)–C(33)	1.51(2)
C(33)–O(5)	1.19(1)	C(33)–O(6)	1.34(2)	C(36)–C(37)	1.50(2)
C(37)–O(7)	1.17(1)	C(37)–O(8)	1.35(1)		
P(1)–Rh(1)–Cl(1)	95.0(1)	P(1)–Rh(1)–C(36)	89.2(3)	Cl(1)–Rh(1)–C(36)	90.2(3)
Rh(1)–P(1)–C(25)	118.1(4)	P(1)–C(25)–C(30)	123.7(8)	C(25)–C(30)–O(4)	121(1)
O(4)–C(32)–C(36)	120(1)	Rh(1)–C(36)–C(32)	122.4(9)	O(4)–C(32)–C(33)	114(1)
C(32)–C(33)–O(5)	124(1)	C(32)–C(33)–O(6)	111(1)	O(5)–C(33)–O(6)	123(1)
Rh(1)–C(36)–C(37)	117.7(9)	C(32)–C(36)–C(37)	118(1)	O(7)–C(37)–C(36)	123(1)
C(36)–C(37)–O(8)	111(1)	O(7)–C(37)–O(8)	124(1)		

18a

Ir(1)–P(1)	2.325(2)	Ir(1)–Cl(1)	2.417(3)	Ir(1)–C(11)	2.05(1)
C(11)–C(14)	1.33(1)	O(5)–C(14)	1.40(1)	O(5)–C(18)	1.38(1)
C(17)–C(18)	1.38(1)	P(1)–C(17)	1.874(10)	C(12)–O(1)	1.19(1)
C(12)–O(2)	1.33(1)	C(15)–O(3)	1.22(1)	C(15)–O(4)	1.30(1)
P(1)–Ir(1)–Cl(1)	94.50(9)	P(1)–Ir(1)–C(11)	89.7(3)	Cl(1)–Ir(1)–C(11)	89.1(3)
Ir(1)–P(1)–C(17)	117.0(3)	P(1)–C(17)–C(18)	124.5(7)	C(17)–C(18)–O(5)	121.4(9)
O(5)–C(14)–C(11)	119.6(9)	Ir(1)–C(11)–C(14)	122.0(8)	Ir(1)–C(11)–C(12)	119.1(7)
C(12)–C(11)–C(14)	118.1(10)	O(1)–C(12)–C(11)	122(1)	C(11)–C(12)–O(2)	112.9(9)
O(1)–C(12)–O(2)	124(1)	O(5)–C(14)–C(15)	115.4(9)	C(11)–C(14)–C(15)	123.9(9)
C(15)–C(14)–O(5)	115.4(9)	O(3)–C(15)–O(4)	121(1)	C(14)–C(15)–O(3)	123(1)
O(4)–C(15)–C(14)	115.2(9)				

18b

Ir(1)–P(1)	2.314(4)	Ir(1)–Cl(1)	2.397(4)	Ir(1)–C(36)	2.08(2)
C(32)–C(36)	1.37(2)	O(4)–C(32)	1.40(2)	O(4)–C(26)	1.40(2)
C(25)–C(26)	1.42(2)	P(1)–C(25)	1.87(1)	C(33)–O(5)	1.16(2)
C(33)–O(6)	1.37(2)	C(37)–O(7)	1.17(2)	C(37)–O(8)	1.37(2)
P(1)–Ir(1)–Cl(1)	93.7(1)	P(1)–Ir(1)–C(36)	89.7(4)	Cl(1)–Ir(1)–C(36)	89.5(5)
Ir(1)–P(1)–C(25)	118.1(5)	P(1)–C(25)–C(26)	123(1)	C(25)–C(26)–O(4)	121(1)
C(26)–O(4)–C(32)	115(1)	O(4)–C(32)–C(36)	119(1)	Ir(1)–C(36)–C(32)	121(1)
O(4)–C(32)–C(33)	119(1)	C(33)–C(32)–C(36)	119(1)	C(32)–C(33)–O(5)	128(2)
C(32)–C(33)–O(6)	107(2)	O(5)–C(33)–O(6)	124(1)	Ir(1)–C(36)–C(37)	120(1)
C(32)–C(36)–C(37)	118(1)	C(36)–C(37)–O(7)	127(1)	O(7)–C(37)–O(8)	125(1)
C(36)–C(37)–O(8)	107(1)				

Table 6 Selected bond lengths (Å) and angles (°) for [Cp*Rh{*P*Ph(C_6H_3-2,6-$(MeO)_2$)(C_6H_3-1-C(C_6H_4-4-COOMe)-*C*)-2-(MeO)-6-(=*O*)}](PF_6) **10b**·$3H_2O$

Rh(1)–P(1)	2.305(2)	Rh(1)–O(3)	2.108(6)	Rh(1)–C(32)	2.017(9)
O(3)–C(26)	1.26(1)	C(25)–C(26)	1.51(1)	P(1)–C(25)	1.946(9)
C(25)–C(30)	1.51(1)	C(26)–C(27)	1.41(1)	C(27)–C(28)	1.35(1)
C(28)–C(29)	1.42(1)	C(29)–C(30)	1.31(1)	C(32)–C(33)	1.34(1)
C(25)–C(33)	1.57(1)				
P(1)–Rh(1)–O(3)	81.1(2)	P(1)–Rh(1)–C(32)	76.2(3)	O(3)–Rh(1)–C(32)	85.5(3)
Rh(1)–P(1)–C(25)	90.1(3)	P(1)–C(25)–C(26)	105.2(6)	C(25)–C(26)–O(3)	118.2(8)
Rh(1)–O(3)–C(26)	118.2(6)	Rh(1)–C(32)–C(33)	120.1(7)	C(32)–C(33)–C(25)	114.5(8)
P(1)–C(25)–C(33)	96.5(6)	O(3)–C(26)–C(27)	122.1(9)		

seven-membered metallacycle derived from the insertion of acetylene dicarboxylate into the metal–O bond. The metal is surrounded by a Cl atom and a P–C bidentate ligand. Figs. 9, 11 and 12 showed that these complexes are Rh_RP_R/Rh_SP_S pairs. The metallacycle is divided into two planes; Rh(1)O(1)C(30)C(31) and Rh(1)P(1)O(1)C(23)C(28) for **9b**,[19] Rh(1)O(4)C(3)C(36) and Rh(1)P(1)O(4)C(25)C(30) for **12b**, Ir(1)O(5)C(11)C(14) and Ir(1)P(1)O(5)C(17)C(18) for **18a** and Ir(1)O(4)C(32)C(36) and Ir(1)P(1)O(4)C(25)C(26) for **18b**; the dihedral angles are 73.4(7), 69.2(5), 69.8(4) and 69.8(5)°, respectively. The fact that the dihedral angles (*ca.* 70°) of complexes bearing sterically bulky phosphine ligand are narrower than that (*ca.* 73°) of **9b** with less bulky phosphine also provides a lager space for the 2,6-$(MeO)_2C_6H_3$ moiety. The dihedral angles between the plane (M–C–C–O) of four atoms containing metal and O atoms and the planes (O=C–O) of the ester groups are 10–15° and 72–78°, respectively, and those between ester groups fall in the range 80–90°, minimizing steric hindrance between ester groups.

Structure of 10b. A perspective drawing of **10b** with an atomic numbring scheme is given in Fig. 7, and selected bond lengths and angles are listed in Table 6. The Rh atom is surrounded by a (P, O, C) tridentate ligand derived from a transannular addition of 1-alkyne between the Rh atom and the *ipso*-carbon atom of the phosphine ligand, accompanying the subsequent transformation of the O donor from the phenoxide to the ketone coordination. The change of this bonding mode causes an elongation of 0.056 Å from 2.050 to 2.106 Å in the Rh–O bond lengths. The molecule has three chiral centers. The priority of order of the ligands is Cp* > P > O > C for a Rh center, Rh > *ipso*-C > 2,6-$(MeO)_2C_6H_3$ > Ph for a P center, and Rh > O > C for an *ipso*-carbon center. Fig. 7 shows that the molecule is a $Rh_RP_SC_S/Rh_SP_RC_R$ pair. The

Table 7 Selected bond lengths (Å) and angles (°) for [Cp*Ir(MDMPP-*P*,*O*){=C(OMe)CH_2Ph}](PF_6) **13a**

Ir(1)–P(1)	2.300(3)	Ir(1)–O(2)	2.103(7)	Ir(1)–C(30)	1.97(1)
C(30)–C(32)	1.56(2)	O(3)–C(30)	1.30(1)	O(2)–C(28)	1.33(1)
C(23)–C(28)	1.40(1)	P(1)–C(23)	1.81(1)		
P(1)–Ir(1)–O(2)	82.4(2)	P(1)–Ir(1)–C(30)	89.5(4)	O(2)–Ir(1)–C(30)	89.5(4)
Ir(1)–P(1)–C(23)	101.1(4)	P(1)–C(23)–C(28)	114.2(8)	C(23)–C(28)–O(2)	121(1)
Ir()–O(2)–C(28)	119.6(7)	Ir(1)–C(30)–O(3)	117.3(9)	Ir(1)–C(30)–C(32)	125.7(8)
O(3)–C(30)–C(32)	116(1)				

Table 8 Selected bond lengths (Å) and angles (°) for [Cp*Rh{*P*Ph_2(C_6H_3-2-(MeO)-6-(OC(COOEt)=*C*(COOEt)))}(CNXyl)](PF_6) **19bcf**

Rh(1)–P(1)	2.350(2)	Rh(1)–C(34)	2.093(8)	Rh(1)–C(38)	1.947(10)
C(30)–C(34)	1.31(1)	O(2)–C(30)	1.413(9)	O(2)–C(28)	1.39(1)
C(23)–C(28)	1.43(1)	P(1)–C(23)	1.811(9)	C(38)–N(1)	1.15(1)
P(1)–Rh(1)–C(34)	87.6(2)	P(1)–Rh(1)–C(38)	92.2(3)	C(34)–Rh(1)–C(38)	94.1(3)
Rh(1)–P(1)–C(23)	118.5(3)	P(1)–C(23)–C(28)	123.3(7)	C(23)–C(28)–O(2)	118.9(8)
O(2)–C(30)–C(34)	120.3(8)	Rh(1)–C(34)–C(30)	118.9(6)	Rh(1)–C(38)–N(1)	172.2(8)
C(38)–N(1)–C(39)	178.7(9)				

carbon atom bearing the 4-substituted phenyl group is connected to the *ipso*-carbon atom as a result of the polarity of the alkyne. The Rh–P length of 2.305(2) Å is not different from those found in related complexes. The Rh(1)–C(32) length of 2.017(9) Å is shorter than that for the complexes described here. The C(32)–C(33) bond length of 1.34(1) Å is indicates C–C double bond. The average length of 1.33 Å for the C(27)–C(28) and C(29)–C(30) double bonds is shorter than that of 1.46 Å for the C(25)–C(26), C(25)–C(30), C(26)–C(27) and C(28)–C(29) single bonds, consisting with a cyclohexadiene ring. The C(26)–O(3) length of 1.26(1) Å is a usual double bond value. The P(1)–Rh(1)–O(3) bite angle of 81.1(2)° and P(1)–Rh(1)–C(32) bite angles of 76.2(3)° in the five-membered rings are narrower than the O(3)–Rh(1)–C(32) bite angle (85.5(3)°) of the six-membered ring.

Structure of 13a. A perspective drawing of **13a** with an atomic numbering scheme is given in Fig. 10. Selected bond lengths and angles are listed in Table 7. The Ir(1)–P(1) and Ir(1)–O(2) bond lengths are essentially the same as those in other complexes. The Ir–C(30) bond length of 1.97 Å is *ca.* 0.10 Å shorter than the Ir–C σ-bond length for **18**, showing the presence of the Ir–C carbene bond. The C(30)–O(3) bond length of 1.30 Å is shorter than usual C–O single bond length, suggesting the presence of electron delocalization in the Ir–C(30)–O(2) moiety.

Structure of 19bcf. A perspective drawing of **19bcf** with an atomic numbering scheme is given in Fig. 13, and selected bond lengths and angles are listed in Table 8. The Rh(1)–P(1) bond length of 2.350(2) Å and Rh(1)–C(34) length of 2.093(8) Å are about 0.05 Å longer than the corresponding lengths in the neutral complex **9b**,[19] as a result of the steric demand of the isocyanide ligand. The Rh(1)–C(38) bond length of 1.947(10) Å is shorter than the Rh(1)–C(34) bond length, as a result of different bonding modes. The C(38)–N(1) bond length of 1.15(1) Å is comparable with a usual C–N triple bond length. The Rh(1)–C(38)–N(1) and C(38)–N(1)–C(39) bond angles are nearly linear

Experimental

All syntheses were carried out under a nitrogen atmosphere. Dichloromethane was distilled over CaH_2 and diethyl ether was distilled over $LiAlH_4$. Isocyanides,[25] phosphines[26] and pentamethylcyclopentadienyl complexes of rhodium[12] and iridium[13] were prepared according to the literature. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 instruments, respectively. The ^{1}H NMR spectra were measuered at 250 MHz, and ^{31}P{^{1}H} NMR spectra were measured at 101 MHz using 85% H_3PO_4 as an external reference. Elemental analyses were performed by Analysical Center, Faculty of Pharmaceutical Department, Toho Univesity.

Reaction of [Cp*$RhCl_2$]$_2$ with BDMPP

A solution of [Cp*$RhCl_2$]$_2$ (1.035 g, 1.67 mmol) and BDMPP (3.21 g, 8.38 mmol) was refluxed in EtOH (10 mL) for 20 h. The solvent was removed and the residue extracted with benzene. After removal of benzene, the residue was chromatographed on deactivated alumina (containing 10% H_2O) using CH_2Cl_2 and ethyl acetate as eluents. The solvent was removed from the reddish brown eluate with CH_2Cl_2 and the residue was washed with diethyl ether to give orange solid **3a** (0.68 g, 34%). The work-up of the eluate with ethylacetate gave orange solid **2a** (1.15 g, 53%). **2a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.51 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 3.08 (s, OMe, 3H), 3.25 (s, OMe, 3H), 3.74 (s, OMe, 3H), 5.8–7.5 (m, ArH, 11H). ^{31}P NMR (100 MHz, $CDCl_3$): δ 55.7 (d, J_{RhP} = 127 Hz). Anal. Calc. for $C_{31}H_{35}O_4$PClRh: C, 58.09; H, 5.50. Found C, 58.10; H, 5.26%. **3a**: UV (CH_2Cl_2): λ_{max} 303 (sh), 235 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.34 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.51 (s, OMe, 6H), 5.7–7.7 (m, ArH, 11H). ^{31}P NMR (100 MHz, $CDCl_3$): δ 36.9 (d, J_{RhP} = 157.5 Hz). Anal.Calc. for $C_{30}H_{35}O_4$PRh: C, 61.02; H, 5.46. Found C, 60.88; H, 5.74%.

Reaction of [Cp*$RhCl_2$]$_2$ with TDMPP

A solution of [Cp*$RhCl_2$]$_2$ (1.06 g, 1.72 mmol) and TDMPP (442 mg, 1.0 mmol) was stirred in MeOH (10 mL) at room temperature. After 50 h, the solvent was removed under reduced pressure and the residue extracted with benzene. Benzene was removed and the residue was washed with diethyl ether to give orange solid **4** (153 mg, 68%). **4**: UV(CH_2Cl_2): λ_{max} 302, 235 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.45 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.42 (s, OMe, 6H), 3.49 (s, OMe, 6H), 5.7–7.6 (m, ArH, 9H). ^{31}P NMR (100 MHz, $CDCl_3$): δ 43.7 (d, J_{RhP} = 137.5 Hz). Anal. Calc. for $C_{32}H_{36}O_6$PRh: C, 59.08; H, 5.58. Found C, 59.33; H, 5.78%.

Reaction of 1a with ethynylbenzene

To a solution of **1a** (50 mg, 0.086 mmol) and PhC≡CH (0.1 mL) in CH_2Cl_2 (15 mL) and acetone (10 mL) was added an excess of $NaPF_6$ at room temperature. After 4 h, the solvent was removed and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 was removed to give an oily product and the residue was chromatographed on silica gel using CH_2Cl_2–*n*-hexane (1 : 5) as an eluant. Reddish brown eluate was dried and the residue recrystallized from CH_2Cl_2–diethyl ether to give orange crystals of **5a** (27 mg, 35%). IR (Nujol): 1591, 1568, 837 cm^{-1}. UV

(CH_2Cl_2): λ_{max} *ca.* 360, 286 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.30 (s, OMe, 3H), 6.3–7.6 (m, CH= and ArH, 25H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 36.9 (d, J_{RhP} = 157.5 Hz), −143.8 (septet, J_{PF} = 717 Hz, PF_6^-). FAB mass (*m*/*z* of cationic part): 749 (749.7). Anal. Calc. for $C_{45}H_{43}O_2P_2F_6Rh$: C, 60.41; H, 4.84. Found C, 60.12; H, 4.83%.

Reddish brown complex **5b** (26 mg, 30%) was prepared by the reaction of **1a** (54.5 mg, 0.095 mmol) with ethynyltoluene (0.2 mL) in the presence an excess of $NaPF_6$ by a procedure similar to that for **5a**. IR (Nujol): 1591, 1568, 837 cm^{-1}. UV (CH_2Cl_2): λ_{max} 344 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.34 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 2.16 (s, Me, 3H), 2.43 (s, Me, 3H), 3.32 (s, OMe, 3H), 6.31 (s, –CH, 1H), 6.42 (s, –CH, 1H), 6.5–7.5 (m, ArH, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 36.8 (d, J_{RhP} = 162 Hz), −143.8 (septet, J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cationic part): 777 (M^+). Anal. Calc. for $C_{47}H_{47}O_2P_2F_6Rh$: C, 61.18; H, 5.13. Found C, 60.94; H, 5.05%.

Reaction of 1a with 1-hexyne

A solution of **1a** (50 mg, 0.086 mmol), 1-hexyne (0.1 mL) and an excess of $NaPF_6$ in CH_2Cl_2–acetone (15 mL/10 mL) was stirred for 4 h. The solvent was evaporated and the residue was extracted with CH_2Cl_2. After the solution was concentrated to 3 mL, diethyl ether was added to give orange crystals of **6** (24 mg, 32%). IR (Nujol): 1660, 1593, 837 cm^{-1}. UV (CH_2Cl_2): λ_{max} *ca.* 390 (sh), 283 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.68 (t, J_{HH} = 6.8 Hz, CH_3, 3H), 1.03 (t, J_{HH} = 6.8 Hz, CH_3, 3H), 1.39 (d, J_{HH} = 2.5 Hz, Cp*, 15H), 1.2–2.8 (m, $(CH_2)_3$, 12H), 3.38 (s, OMe, 3H), 5.56 (s, CH=, 1H), 5.69 (d, J_{RhH} = 15.0 Hz, 1H), 6.6–7.8 (m, ArH, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 44.8 (d, J_{RhP} = 157.5 Hz), −143.8 (septet, J_{PF} = 712 Hz, PF_6^-). Anal. Calc. for $C_{41}H_{51}O_2P_2F_6Rh$: C, 57.62; H, 6.01. Found C, 57.65; H, 5.85%.

Reaction of 1a with 1-ethynyl-4-methoxycarbonylbenzene

A solution of **1a** (139 mg, 0.24 mmol), $HC{\equiv}CC_6H_4COOMe$-4 (107.4 mg, 0.67 mmol) and KPF_6 (144 mg, 0.78 mmol) in CH_2Cl_2 (5 mL) and acetone (20 mL) was stirred at room temperature. After 25 h, the solvent was removed and the residue was extracted with CH_2Cl_2 and a solution of CH_2Cl_2 was filtered with a glass filter (G4). The solvent was removed under reduced pressure. The residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give red crystals of **5c** (39 mg, 20%) and black brown crystals of **7** (57 mg, 24%). **5c**: IR (Nujol): 1717(C=O), 839 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 387, 290 (sh), 239 nm. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.36 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.35 (s, OMe, 3H), 3.88 (s, COOMe, 3H), 3.95 (s, COOMe, 3H), 6.49 (d, J_{HH} = 8.5Hz, =CH, 1H), 8.19 (d, J_{HH} = 8.5 Hz, =CH, 1H), 6.5–7.7 (m, ArH, 21H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 35.8 (d, J_{RhP} = 157.5 Hz), −144.8 (sept, J_{PF} = 712 Hz). Anal. Calc. for $C_{49}H_{47}O_6P_2F_6Rh$: C, 58.22; H, 4.69. Found C, 58.14; H, 4.58%. **7**: IR (Nujol): 3285 (O–H), 1717 (C=O), 1605 (C=C), 839 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 404, 279 nm. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.41 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 3.44 (s, OMe, 3H), 3.83 (s, COOMe, 3H), 6.74 (s, OH, 1H), 5.8–8.0 (m, ArH, 17H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 29.7 (d, J_{RhP} = 136.5 Hz). Anal. Calc. for $C_{39}H_{40}O_4PCl_2Rh{\cdot}CH_2Cl_2$: C, 55.71; H, 4.91. Found C, 55.10; H, 4.92%.

Reaction of 1a with methylpropiolate

A solution of **1a** (110 mg, 0.189 mmol), HC≡CCOOMe (0.1 mL) and an excess of $NaPF_6$ in CH_2Cl_2 (5 mL) and acetone (10 mL) was stirred at room temperature. After 5 h, the solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2. The solvent was removed. The residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give yellow orange crystals of **8a** (61 mg, 40%). IR (Nujol): 2060, 1699, 1583, 839 cm^{-1}. UV (CH_2Cl_2): λ_{max} 293 nm. ^{1}H MNR (250 MHz, $CDCl_3$): δ 1.54 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.16 (s, OMe, 3H), 3.76 (s, OMe, 3H), 6.7–7.8 (c, ArH, 13H), 7.96 (s, CH=, 1H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.12 (d, J_{RhP} = 122 Hz), −143.9 Hz (septet. J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cation part): 658 (675.4). Anal. Calc. for $C_{34}H_{35}O_5P_2F_6Rh$: C, 51.14; H, 4.31. Found C, 50.89; H, 4.40%. Yellow complex **8b** (32%) was obtained from **1** with HC≡CCOOEt by a procedure similar to that for **8a**. IR (Nujol): 2060 (C≡O), 1695 (C=O), 837 (PF_6) cm^{-1}. UV (CH_2Cl_2): λ_{max} 310 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (t, J_{HH} = 7.5 Hz, Me, 3H), 1.54 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.16 (s, OMe, 3H), 4.22 (q, J_{HH} = 7.5 Hz, OCH_2, 2H), 6.7–7.8 (m, ArH, 13H), 7.96 (s, CH=, 1H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.15 (d, J_{RhP} = 125 Hz), −143.9 (septet, J_{PF} = 711.0 Hz, PF_6^-). Anal. Calc. for $C_{35}H_{37}O_5P_2F_6Rh$: C, 51.80; H, 4.51. Found C, 51.48; H, 4.57%.

Reaction of 1a with EtOOCC≡CCOOEt

Reddish orange crystals **9b** (45 mg, 63%) were obtained from **1a** (55 mg, 0.095 mmol), EtOOCC≡CCOOEt (0.1 mL) and an excess of $NaPF_6$ by a procedure similar to that for **8a**. IR (Nujol): 1705 (C=O), 1589 (C=C) cm^{-1}. UV (CH_2Cl_2): λ_{max} *ca.* 400(sh), 328 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.03 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.27 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.26 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 3.03 (s, OMe, 3H), 4.03 (m, CH_2, 2H), 4.18 (m, CH_2, 2H), 7.0–7.9 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 10.3 (d, J_{RhP} = 137 Hz, 1P). FAB mass (*m*/*z* of cation part): 737 ([M − CO]$^+$). Anal. Calc. for $C_{37}H_{41}O_6PClRh{\cdot}0.5CH_2Cl_2$: C, 56.76; H, 5.34. Found C, 56.56; H, 5.22%. **9a** (57%) was obtained from the reaction between **1a** (30 mg, 0.052 mmol), MeOOCC≡CCOOMe (0.15 mL) and $NaPF_6$ (24 mg, 0.14 mmol). IR (Nujol): 1705 (C=O), 1581 (C=C) cm^{-1}. UV (CH_2Cl_2): λ_{max} 364, 266 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 3.04 (s, OMe, 3H), 3.53 (s, OMe, 3H), 3.74 (s, OMe, 3H), 5.28 (s, CH_2Cl_2, 2H), 6.6–7.7 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 10.3 (d, J_{RhP} = 137.5 Hz, 1P). FAB mass (*m*/*z* of cation part): 709 ([M − CO]$^+$). Anal. Calc. for $C_{35}H_{37}O_6PClRh{\cdot}0.5CH_2Cl_2$: C, 55.70; H, 5.00. Found C, 55.20; H, 4.75%.

Reaction of 2a with 1-ethynyl-4-methoxycarbonylbenzene

A solution of **2a** (45.7 mg, 0.071 mmol), $HC{\equiv}CC_6H_4COOMe$-4 (37.6 mg, 0.235 mmol) and KPF_6 (37.2 mg, 0.202 mmol) in CH_2Cl_2 (5 mL) and acetone (20 mL) was stirred at room temperature. After 8 h, the solvent was removed and the residue was extracted with CH_2Cl_2 and a solution of CH_2Cl_2 was filtered with a glass filter (G4). The solvent was removed under reduced pressure. The residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give yellow solid **10a** (27.8 mg, 43%). IR (Nujol): 1715 (C=O), 1630 (C=O) and 839 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 405, 284 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.74 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.97 (s, OMe, 3H), 3.06 (bs, OMe, 6H), 3.48 (bs, OMe, 3H), 3.84 (s, COOMe, 3H), 5.59 (d, J_{RhH} = 7.0 Hz, CH=, 1H) 5.6–7.2 (m, ArH, 15H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.7 (d, J_{RhP} = 153 Hz), −143.7 (septet, J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cation part): 765 ([M − 1]$^+$), 605 ([M − (HC=C_6H_5COOMe)]$^+$). Anal. Calc. for $C_{41}H_{43}O_6P_2F_6Rh$: C, 54.08; H, 4.76. Found C, 53.82; H, 4.81%. Brown complex **10b** (18%) was obtained from the reaction of **2a** and $HC{\equiv}CC_6H_4NO_2$-4. IR (Nujol): 1628 (C=O), 835 (PF_6) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.74 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.99 (s, MeO, 3H), 3.08 (br, MeO, 3H), 3.52 (br, MeO, 3H), 5.68 (d, J_{RhH} = 7.5 Hz, CH=, 1H), 6.4–8.2 (m, Ph and ring Protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 140.4 (d, J_{RhH} = 153 Hz), −143.7 (septet, J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cation part): 752 ([M − PF_6]$^+$), 605 ([M − PF_6 − HC=$CC_6H_4NO_2$]$^+$). Anal. Calc. for $C_{39}H_{40}NO_6P_2F_6Rh{\cdot}CH_2Cl_2$: C, 48.90; H, 4.31; N, 1.43. Found C, 49.19; H, 4.40; N, 1.52%.

Reaction of 2a with methylpropiolate

Yellow crystals of **11a** were prepared by the reaction of **2a** (40.8 mg, 0.064 mmol), KPF_6 (39.0 mg, 0.212 mmol) and HC≡CCOOMe (0.05 mL, 0.60 mmol) at room temperature for 9 h, according to a procedure similar to that for **8a**. IR (Nujol): 2064, 1694, 841 cm^{-1}. UV (CH_2Cl_2): λ_{max} 298 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.62 (d, J_{PH} = 3.8 Hz, Cp*, 15H), 3.24 (s, OMe, 3H), 3.31 (s, OMe, 3H), 3.68 (s, OMe, 3H), 3.85 (s, COOMe, 3H), 6.5–7.7 (m, ArH, 11H), 7.92 (s, CH=, 1H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −13.4 (d, J_{RhP} = 126.5 Hz), −143.8 (septet. J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cation part): 717 ($[M - 1]^+$), 689 ($[M - CO]^+$), 605 (M − CO − (CH=CCOOMe)]$^+$). Anal. Calc. for $C_{36}H_{39}O_7P_2F_6Rh$: C, 50.13; H, 4.56. Found C, 49.89; H, 4.41%.

Brown complex **11b** (15 mg, 33%) was obtained by the reaction of **2a** (33.2 mg, 0.052 mmol), KPF_6 (29.4 mg, 0.160 mmol) and HC≡CCOOEt (0.05 mL, 0.489 mmol) at room temperature for 4 h, according to a procedure similar to that for **8a**. IR (Nujol): 2062 (CO), 1688 (C=O), 841 cm^{-1}. UV (CH_2Cl_2): λ_{max} 298, 232 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.33 (t, J_{HH} = 7.0Hz, Me, 3H), 1.59 (d, J_{PH} = 4.0 Hz, Cp*, 15H), 3.22 (s, OMe, 3H), 3.28 (s, OMe, 3H), 3.64 (s, OMe, 3H), 4.28 (q, J_{HH} = 7.0 Hz, CH_2, 2H), 6.5–7.7 (c, ArH, 11H), 7.90 (s, CH=, 1H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −13.5 (d, J_{RhP}, 132 Hz), −143.8 Hz (septet, J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z* of cation part): 731 ($[M - 1]^+$), 703 ($[M - CO + 1]^+$), 605 (M–CO–(CH=CCOOEt)]$^+$). Anal. Calc. for $C_{37}H_{41}O_7P_2F_6Rh$: C, 50.70; H, 4.71. Found C, 50.92; H, 4.55%.

Reaction of 2a with MeOOCC≡CCOOMe

Reddish orange crystals **12a** (47.3 mg, 56%) were obtained from **2** (69.6 mg, 0.109 mmol), MeOOCC≡CCOOMe (0.2 mL, 1.63 mmol) and KPF_6 (61.2 mg, 0.333 mmol) at room temperature for 5 h by a procedure similar to that for **9b**. IR (Nujol): 1707 (C=O) cm^{-1}. UV (CH_2Cl_2): λ_{max} 371, 274 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.34 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 3.07 (s, OMe, 3H), 3.23 (s, OMe, 3H), 3.58 (s, OMe, 3H), 3.77(s, COOMe, 3H), 6.3–7.6 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −1.92 (d, J_{RhP} = 151.5 Hz, 1P). FAB mass (*m*/*z*): 782 ($[M - 1]^+$), 747 ($[M - Cl - 1]^+$), 605 ($[M - Cl - (MeOOCC-COOMe)]^+$). Anal. Calc. for $C_{37}H_{41}O_8PClRh$: C, 56.75; H, 5.28. Found C, 56.35; H, 5.34%. Complex **12b** (45.3 mg, 47%) was prepared by the reaction of **2a** (76.5 mg, 0.119 mmol), MeOOCC≡CCOOMe (0.2 mL, 1.26 mmol) and KPF_6 (60.5 mg, 0.329 mmol) at room temperature for 44 h by a procedure similar to that for **9b**. IR (Nujol): 1703 (C=O) cm^{-1}. UV (CH_2Cl_2): λ_{max} 371, 273 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.34 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 3.07 (s, OMe, 3H), 3.22 (s, OMe), 3.58 (s, OMe), 4.18–4.27 (m, $COOCH_2Me$, 2H), 6.3–7.6 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −2.02 (d, J_{RhP} = 151.0 Hz, 1P). FAB mass (*m*/*z*): 811 ($[M]^+$), 641 ($[M - (EtOOCC=CCOOEt)]^+$), 605 ($[M - Cl - (EtOOCC=CCOOEt)]^+$). Anal. Calc. for $C_{39}H_{45}O_8PClRh$: C, 57.75; H, 5.59. Found C, 57.41; H, 5.59%.

Reaction of 1b with ethynylbenzene

To a solution of **1b** (122 mg, 0.182 mmol) and PHC≡CH (0.25 mL, 2.28 mmol) in CH_2Cl_2 (5 mL) and MeOH (20 mL) was added KPF_6 (151.2 mg, 0.82 mmol) at room temperature. After 24 h, the solvent was removed and the residue extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2 and diethyl ether to give pale yellow crystals of **14** (25.2 mg, 17%). The solvent was removed from the mother-liquor and the residue was recrystallized from CH_2Cl_2 and diethyl ether to give yellow crystals of **13a** (45 mg, 27%) **13a**: IR (Nujol): 837 cm^{-1}. UV (CH_2Cl_2): λ_{max} 322, 232 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.46 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 3.37 (s, OMe, 3H), 3.83 (s, =COMe, 3H), 4.13 (s, CH_2, 1H) 4.18 (s, CH_2, 1H), 6.0–7.7 (m, ArH, 18H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.1 (s), −143.7 (septet, J_{PF} = 712 Hz, PF_6^-). Anal. Calc. for $C_{38}H_{41}O_3P_2F_6Ir$: C, 49.94; H, 4.52. Found C, 49.68; H, 4.51%.

Complex **13b** together with a small amount of **14** was obtained from the reaction between **1b** and the corresponding 1-alkyne in the presence of KPF_6, according to a procedure similar to that of **13a**. **13b**: IR (Nujol): 837 cm^{-1}. UV (CH_2Cl_2): λ_{max} 328 nm. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.48 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 2.31 (s, Me, 3H), 3.38 (s, OMe, 3H), 3.75 (s, =COMe, 3H), 4.15 (s, CH_2, 1H), 4.21 (s, CH_2, 1H), 6.1–7.8 (m, ArH, 18H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.8 (s), −144.7 (septet, J_{PF} = 712 Hz, PF_6^-).

Reaction of 1b with 1-ethynyl-4-methoxycarbonylbenzene

A solution of **1b** (144.8 mg, 0.216 mmol), HC≡CC_6H_4COOMe-4 (72.9 mg, 0.455 mmol) and KPF_6 (105.3 mg, 0.572 mmol) in CH_2Cl_2 (5 mL) and acetone (20 mL) was stirred at room temperature. After 24 h, the solvent was removed and the residue extracted with CH_2Cl_2 and a solution of CH_2Cl_2 was filtered with a glass filter. The solvent was removed under reduced pressure. The residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give orange crystals of **16** (25 mg, 14%). Work-up of the mother-liquor and recrystallization from CH_2Cl_2 and diethyl ether gave orange crystals of **15** (67 mg, 28%). **15**: IR (Nujol): 3312 (OH), 1717 (C=O) cm^{-1}. UV (CH_2CI_2: λ_{max} 271 nm. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.44 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 3.45 (s, OMe, 3H), 3.84 (s, COOMe, 3H), 6.64 (s, OH, 1H), 5.8–8.0 (m, ArH, 17H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 3.54 (s). Anal. Calc. for $C_{39}H_{40}O_4PCl_2Ir{\cdot}CH_2Cl_2$: C, 50.48; H, 4.65. Found C, 50.38; H, 4.53%. **16**: IR (Nujol): 1721(C=O), 843 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 325(sh), 270(sh) nm. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.29 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 3.67 (s, OMe, 3H), 3.89 (s, COOMe, 3H), 3.90 (s, COOMe, 3H), 5.2–7.9 (m, CH= and ArH, 21H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 21.9 (s), −143.8 (septet, J_{PF} = 712 Hz, PF_6^-). FAB mass (*m*/*z*): 955 ($[M]^+$), 794 ($[M - (CH=CC_6H_4COOMe) - 1]^+$), 635 ($[M - (CH=CC_6H_4COOMe)_2]^+$). Anal. Calc. for $C_{49}H_{47}O_6P_2F_6Ir$: C, 53.50; H, 4.31. Found C, 53.14; H, 4.48%.

Reaction of 1b with MeOOCC≡CCOOMe

Yellow crystals of 17a (34.7 mg, 44%) were obtained from **1b** (65.3 mg, 0.097 mmol), MeOOCC≡CCOOMe (0.15 mL, 1.22 mmol)) and KPF_6 (72 mg, 0.391 mmol) by a procedure similar to that for **8a**. IR (Nujol): 1703 (C=O). UV (CH_2Cl_2): λ_{max} 294(sh) nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.28 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 3.03 (s, OMe, 3H), 3.62 (s, COOMe, 3H), 3.76 (s, COOMe, 3H), 6.6–7.7 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −23.8 (s). Anal. Calc. for $C_{35}H_{37}O_6PClIr$: C, 51.75; H, 4.59. Found C, 50.35; H, 4.62%.

Analogously, complexes **17b**, **18a** and **18b** were prepared from the corresponding compounds, according to a procedure similar to that for **8a**. **17b**: IR (Nujol): 1698 (C=O) cm^{-1}. UV (CH_2Cl_2): λ_{max} 291(sh) nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.12 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.28 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 1.30 (t, J_{HH} = 7.0 Hz, Me, 3H), 3.03 (s, OMe, 3H), 4.0–4.25 (m, CH_2, 4H), 6.5–7.7 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −24.0 (s). Anal. Calc. for $C_{37}H_{41}O_6PClIr$: C, 52.88; H, 4.92. Found C, 52.99; H, 5.20%. **18a** (yellow, 68%) IR (Nujol): 1709 (C=O) cm^{-1}. UV (CH_2Cl_2): λ_{max} 288 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.31 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 3.02 (s, OMe, 3H), 3.20 (s, OMe, 3H), 3.56 (s, OMe, 3H), 3.75 (s, COOMe, 3H), 3.77 (s, COOMe, 3H), 6.3–7.7 (m, Ph, 11H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −36.4 (s). FAB mass (*m*/*z* of cation part): 872 ($[M]^+$), 837 ($[M - Cl]^+$), 695 ($[M - Cl - MeOOC=CCOOMe)]^+$). Anal. Calc. for $C_{37}H_{41}O_8PClIr$: C, 50.94; H, 4.74. Found C, 50.97; H, 4.74%. **18b** (yellow, 28%): IR (Nujol): 1709, 1694 (C=O) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.32 (t,

J_{HH} = 7.0 Hz, Me, 3H), 1.34 (d, J_{PH} = 2.0 Hz, Cp*, 15H), 1.35 (d, J_{HH} = 7.0 Hz, Me, 3H), 3.04 (s, OMe, 3H), 3.22 (s, OMe, 3H), 3.58 (s, OMe, 3H) 4.15–4.33 (m, CH_2, 4H), 6.5–7.7 (m, Ph, 11H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −36.2 (s). Anal. Calc. for $C_{39}H_{45}O_8PCIr$: C, 52.02; H, 5.04. Found C, 52.36; H, 5.20%.

Reactions of 9 with Lewis bases

(a) With xylyl isocyanide in the presence of KPF_6. A solution of **9a** (74.7 mg, 0.103 mmol), xylyl isocyanide (45 mg, 0.343 mmol) and KPF_6 (64.8 mg, 0.352 mmol) in CH_2Cl_2 (25 mL) and acetone (20 mL) was stirred at room temperature for 24 h. After the solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2. After CH_2Cl_2 was removed, the residue was washed with diethyl ether and recrystallized from CH_2Cl_2 and diethyl ether to give yellow crystals of **19ace** (87.3 mg, 88%). IR (Nujol): 2159 (N≡C), 1734 (C=O), 837 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 313(sh), 235 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.51 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.01 (s, *o*-Me, 6H), 3.22 (s, OMe, 3H), 3.79 (s, COOMe, 3H), 3.83 (s, COOMe, 3H), 6.6–7.9 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 7.16 (s), −143.8 (septet, J_{PF} = 712 Hz, PF_6^-). Anal. Calc. for $C_{44}H_{46}NO_6F_6P_2Rh$: C, 54.84; H, 4.81; N, 1.45. Found C, 54.64; H, 4.79; N, 1.54%.

(b) With xylyl isocyanide or mesityl isocyanide in the presence of Ag(OTf). A solution of **9a** (146.4 mg, 0.203 mmol), xylyl isocyanide (55.5 mg, 0.423 mmol) and Ag(OTf) (52.6 mg, 0.205 mmol) in CH_2Cl_2 (5 mL) and acetone (15 mL) was stirred at room temperature for 24 h. The work-up similar to that for **19ace** gave yellow crystals of **19acf** (55.8 mg, 28%). IR (Nujol): 2159 (N≡C), 1717 (C=O), 1209 (OTf), 1030 (OTf), 635 (OTf) cm^{-1}. UV (CH_2Cl_2): λ_{max} 314(sh), 235 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.51 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.09 (s, *o*-Me, 6H), 3.22 (s, OMe, 3H), 3.78 (s, COOMe, 3H), 3.81 (s, COOMe, 3H), 6.6–7.8 (m, Ph, 16H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 6.4 (d, J_{RhP} = 127 Hz). Anal. Calc. for $C_{44}H_{46}NO_9F_3PSRh$: C, 55.85; H, 4.79; N, 1.45. Found C, 55.74; H, 4.82; N, 1.54%. **19adf** (yellow, 57%): a procedure similar to that for **19ace** was carried out except the reaction time of 5 h. IR (Nujol): 2153 (N≡C), 1719 (C=O), 1703 (C=O), 1032 (OTf), 637 (OTf) cm^{-1}. UV (CH_2Cl_2): λ_{max} 312 (sh), 245 nm. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.50 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.04 (s, *o*-Me, 6H), 2.29 (s, *p*-Me, 3H), 3.22 (s, OMe, 3H), 3.78 (s, COOMe, 3H), 3.80 (s, COOMe, 3H), 6.7–7.9 (m, Ph, 15H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 6.45 (d, J_{RhP} = 127.5 Hz). Anal. Calc. for $C_{46}H_{48}NO_9F_3PSRh$: C, 56.27; H, 4.93; N, 1.43. Found C, 56.30; H, 5.46; N, 1.36%. **19bcf** (yellow, 85%): A procedure similar to that for **19ace** was carried out except the reaction time of 5 h. IR (Nujol): 2153 (N≡C), 1725 (C=O), 1705 (C=O), 1032 (OTf), 637 (OTf) cm^{-1}. UV (CH_2Cl_2): λ_{max} 312 (sh), 235 nm ^1H NMR (250 MHz, CD_2Cl_2): δ 1.26 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.33 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.53 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.05 (s, *o*-Me, 6H), 3.22 (s, OMe, 3H), 4.23 (q, CH_2, J_{HH} = 7.0 Hz, 4H), 6.6–7.9 (m, Ph, 16H). $^{31}P\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 7.16 (d, J_{RhP} = 127 Hz). Anal. Calc. for $C_{47}H_{50}NO_9F_3PSRh$: C, 56.69; H, 5.06; N, 1.41. Found C, 56.41; H, 5.06; N, 1.49%. **19bdf** (yellow, 38%): A procedure similar to that for **19ace** was carried out except the reaction time of 5 h. IR (Nujol): 2151 (N≡C), 1717 (C=O), 1696 (C=O), 1034 (OTf), 637 (OTf) cm^{-1}. UV (CH_2Cl_2): λ_{max} 315 (sh), 238 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.26 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.33 (t, J_{HH} = 7.0 Hz, Me, 3H), 1.52 (d, J_{PH} = 3.5 Hz, Cp*, 15H), 2.00 (s, *o*-Me, 6H), 2.28 (s, *p*-Me, 3H), 3.23 (s, OMe, 3H), 4.23 (q, J_{HH} = 7.0 Hz, CH_2, 4H), 6.6–7.9 (m, Ph, 15H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 7.21 (d, J_{RhP} = 127 Hz). Anal. Calc. for $C_{48}H_{52}NO_9F_3PSRh$: C, 52.45; H, 4.77; N, 1.27. Found C, 52.41; H, 5.00; N, 1.37%.

(c) With carbon monoxide in the presence of Ag(OTf). Carbon monoxide was bubled into a solution of **9a** (153.3 mg, 0.212 mmol) and Ag(OTf) (202.7 mg, 0.789 mmol) in CH_2Cl_2 (25 mL) and acetone (25 mL) at room temperature for 3 min. After 5 h, work-up similar to that for 19ace gave yellow solid **20a** (158.2 mg, 69%). IR (Nujol): 2068 (C≡O), 1715 (C=O), 1028, 637, 573 (OTf) cm^{-1}. UV (CH_2Cl_2): λ_{max} 303(sh), 235 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.60 (d, J_{PH} = 4.0 Hz, Cp*, 15H), 3.18 (s, OMe, 3H), 3.75 (s, COOMe, 3H), 3.82 (s, COOMe, 3H), 6.7–7.8 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 3.31 (d, J_{RhP} = 122 Hz).

Preparation of 21

(a) With 1a and MeOOCC≡CCOOMe in the presence of Ag(OTf). A solution of **1a** (143.6 mg, 0.25 mmol), MeOOCC≡CCOOMe (0.25 mL, 2.04 mmol) and Ag(OTf) (131.4 mg, 0.511 mmol) in MeOH (20 mL) and CH_2Cl_2 (5 mL) was stirred for 7 h at room temperature. The solvent was removed under reduced pressure. The oily product was chromatographed on alumina (contained 10% H_2O) using ethyl acetate as an eluent. The eluting solution was concentrated and the residue recrystallized from CH_2Cl_2 and diethyl ether to give orange crystals **21** (63.2 mg, 26%). IR (Nujol): 1732, 1709 (C=O), 841 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 288(sh), 236 nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.48 (d, J_{PH} = 3.0 Hz, Cp*, 15H), 2.79 (s, OMe, 3H), 3.44 (s, COOMe, 3H), 3.55 (s, COOMe, 3H), 3.92 (s, COOMe, 3H), 4.05 (s, COOMe, 3H), 6.7–7.7 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −35.3 (d, J_{RhH} = 148 Hz). FAB mass (*m*/*z* of cationic part): 828 ($[M - 1]^+$), 545 ($[M - (MeOOCC{\equiv}CCOOMe)_2]^+$). Anal. Calc. for $C_{42}H_{43}O_{13}F_3PSRh$: C, 49.96; H, 4.29. Found C, 50.00; H, 4.39%.

(2) With 9a and MeOOCC≡CCOOMe in the presence of Ag(OTf). Complex **21** was generated from **9a** and MeOOCC≡CCOOMe in the presence of Ag(OTf) according to a procedure similar to (a).

Reaction of [Cp*Ir(CO)(MDMPP-*P*,*O*)](PF_6) 14 with MeOOCC≡CCOOMe

(a) In MeOH. A solution of **14** (138 mg, 0.17 mmol) and MeOOCC≡CCOOMe (0.25 mL, 2.04 mmol) in MeOH (40 mL) was refluxed for 20 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give [Cp*Ir(CO)-($PPh_2(C_6H_3$-2-(MeO)-6-(OC(COOMe)=*C*(COOMe))][PF_6) **22** (86.6 mg, 44%). IR (Nujol): 2066 (C≡O), 1717 (C=O), 841 (P–F) cm^{-1}. UV (CH_2Cl_2): λ_{max} 298(sh), 269(sh) nm. ^1H NMR (250 MHz, $CDCl_3$): δ 1.65 (d, J_{PH} = 2.5 Hz, Cp*, 15H), 3.16 (s, OMe, 3H), 3.76 (s, COOMe, 3H), 3.82 (s, COOMe, 3H), 6.7–7.8 (m, Ph, 13H). $^{31}P\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ −36.6 (s), −143.9 (septet, J_{PF} = 172 Hz, PF_6^-). FAB mass (*m*/*z* of cationic part): 804 ($[M]^+$), 775 ($[M - CO + 2]^+$), 635 ($[M - CO - (MeOOCC{=}CCOOMe)]^+$). Anal. Calc. for $C_{38}H_{41}O_8F_6P_2Ir$: C, 45.92; H, 4.16. Found C, 45.88; H, 4.09%.

(b) In CH_2Cl_2. Complex **17a** (38%) was obtained from [Cp*Ir(CO)(MDMPP-*P*,*O*)](PF_6) **14** and MeOOCC≡CCOOMe in CH_2Cl_2 at reflux for 8 h.

(c) In MeOH and CH_2Cl_2. Complexes **17a** (23%) and **22** (17%) were obtained from **14** (69.0 mg, 0.09 mmol) and MeOOCC≡CCOOMe (0.13 mL, 1.02 mmol) in MeOH (15 mL) and CH_2Cl_2 (15 mL) at reflux for 10 h.

Data collection

All complexes were recrystallized from acetone–diethyl ether or CH_2Cl_2–diethyl ether. Cell constants were determined from 20–25 reflections on a Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collections are summarized in Table 9. Data collections were carried out on

Table 9 Crystal data for [Cp*RhCl(BDMPP-*P*,*O*)] **2a**, [Cp*Rh(TDMPP-*P*,*O*,*O*′)] **4a**, [Cp*Rh{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*C(Tol)=CHCH=*C*(Tol))}](PF$_6$) **5b**, [Cp*Rh{PPh$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*C(C$_6$H$_4$-4-COOMe)=CHCH=*C*(C$_6$H$_4$-4-COOMe)))}](PF$_6$) **5c**, [Cp*Rh{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(*O*C(*n*Bu)CH=CC(*n*Bu)=*C*H))}][(PF$_6$) **6**, [Cp*Rh(CO){*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(OCH=*C*(COOMe)))}](PF$_6$) **8a**, [Cp*Rh(BDMPP-*P*,*O*)-(HC≡CC$_6$H$_4$NO$_2$)] (PF$_6$) **10b**·3H$_2$O, [Cp*Rh(CO){*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(O-CH=*C*(COOMe)))}](PF$_6$) **11a**, [Cp*RhCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOR)=*C*(COOR)))] **12b**, [Cp*Ir(MDMPP-*P*,*O*){=C(OMe)CH$_2$R}](PF$_6$) **13a**, [Cp*IrCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOMe)=*C*(COOMe)))] **18a**, [Cp*IrCl{*P*Ph(C$_6$H$_3$-2,6-(MeO)$_2$)(C$_6$H$_3$-2-(MeO)-6-(OC(COOEt)=*C*(COOEt)))] **18b** and [Cp*Rh{*P*Ph$_2$(C$_6$H$_3$-2-(MeO)-6-(OC(COOEt)=*C*(COOEt)))}(CNXyl)](PF$_6$) **19bcf**

Compound	**2a**	**4a**	**5b**	**5c**	**6**	**8a**	**10b**·3H$_2$O	**11a**	**12b**	**13a**	**18a**	**18b**	**19bcf**
Formula	C$_{31}$H$_{35}$O$_4$PClRh	C$_{32}$H$_{36}$O$_6$PRh	C$_{47}$H$_{47}$O$_2$P$_2$F$_6$Rh	C$_{49}$H$_{47}$O$_6$P$_2$F$_6$Rh	C$_{41}$H$_{51}$O$_2$P$_2$F$_6$Rh	C$_{34}$H$_{35}$O$_5$P$_2$F$_6$Rh	C$_{39}$H$_{46}$NO$_9$P$_2$F$_6$Rh	C$_{36}$H$_{39}$O$_7$P$_2$F$_6$Rh	C$_{39}$H$_{45}$O$_8$PClRh	C$_{38}$H$_{41}$O$_3$P$_2$F$_6$Ir	C$_{37}$H$_{41}$O$_8$PClIr	C$_{39}$H$_{45}$O$_8$PClIr	C$_{47}$H$_{50}$NO$_9$PF$_3$SRh
Mol. wt	640.95	650.51	922.73	1010.75	854.7	802.49	951.64	862.54	811.11	913.3	862.54	900.43	995.85
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$Pbcn$ (no. 60)	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)	$P1$ (no. 2)	$P2_1/a$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/o$ (no. 14)
a/Å	16.018(7)	17.507(6)	15.74(1)	15.534(3)	11.575(4)	15.411(3)	15.299(7)	10.797(7)	12.031(7)	15.060(9)	11.049(3)	12.515(8)	11.146(4)
b/Å	10.46(1)	21.180(7)	17.42(1)	19.986(3)	16.67(1)	22.199(4)	14.826(7)	24.881(8)	17.48(1)	13.360(8)	16.085(3)	12.00(2)	14.634(3)
c/Å	17.695(4)	15.903(8)	16.32(1)	15.757(3)	10.800(5)	10.602(4)	19.505(9)	14.146(6)	18.152(4)	18.705(9)	19.689(4)	25.04(2)	28.41(2)
α/°	90.0	90.0	90.0	90.0	90.17(5)	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
β/°	94.06(3)	90.0	102.66(6)	103.70(1)	99.46(3)	110.11(3)	106.78(3)	96.16(4)	99.39(3)	90.84(4)	96.17(2)	95.29(8)	91.75(4)
γ/°	90.0	90.0	90.0	90.0	93.41(4)	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
V/Å^3	2957(3)	5896(3)	4364(5)	4752(1)	2051(1)	3405(1)	4235(3)	3778(2)	3766(3)	3763(3)	3478(1)	3834(6)	4631(3)
Z	5	8	4	4	2	4	4	4	4	4	4	4	4
D_{ca}/g cm^{-3}	1.440	1.465	1.404	1.413	1.383	1.565	1.492	1.430	1.430	1.613	1.665	1.560	1.428
μ/cm^{-1}	7.54	6.75	5.26	4.96	5.53	6.68	5.57	6.11	6.16	37.08	40.23	36.53	5.15
Scan rate/° min^{-1}	16	8	4	8	12	16	8	8	8	16	8	16	8
No. of reflections ($\theta < 50°$)	7159	7436	6478	8645	5376	6737	7733	6654	6871	6628	6362	6742	8517
No. of data used	3700 ($I > 3.0\sigma(I)$)	3805 ($I > 3.0\sigma(I)$)	1421 ($I > 2.0\sigma(I)$)*	3298 ($I > 2.0\sigma(I)$)	2310	5172 ($I > 2.0\sigma(I)$)	4458 ($I > 2.0\sigma(I)$)	3228 ($I > 2.0\sigma(I)$)	3189 ($I > 2.0\sigma(I)$)	4500 ($I > 2.0\sigma(I)$)	5967 ($I > 0.0\sigma(I)$)	4121 ($I > 2.0\sigma(I)$)	5118 ($I > 2.5\sigma(I)$)
No. of variables	343	361	238	577	472	433	523	469	451	451	433	451	553
R; R_w[a,b] $R1$(reflections)	0.052; 0.054	0.053; 0.072	0.100; 0.107	0.063; 0.075	0.072; 0.075	0.050; 0.069	0.101; 0.156 0.066(4458)	0.086; 0.142	0.058; 0.072	0.070; 0.121 0.044(4500)	0.084; 0.083 0.039(4354)	0.089; 0.144 0.053 (4121)	0.073; 0.092
GOF[c]	1.25	2.24	1.82	1.22	1.28	1.87	2.30	3.15	1.62	1.98	1.41	1.78	3.21

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). [b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$ and $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$); $R1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$. [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

a Rigaku AFC5S refractometer at 27 °C. Intensities were measured by the 2θ–ω scan method using Mo-Kα radiation (λ = 0.71069 Å). Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were made with ψ scans. Atomic scattering factors were taken from Cromer and Waber the usual tabulation.[27] Anomalous dispersion effects were included in F;[28] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[29] All calculations were performed using the teXsan crystallographic software package.[30]

Determination of the structures

The structures were solved by Patterson methods (DIRDIF92 PATTY) and refined on F values except for **10b**, **18a** and **18b** refined on F^2 values, since these three complexes were not well-refined on F values. All non-hydrogen atoms were isotropically refined except the rhodium atom refined with anisotropic thermal parameters in **5b**, because of poor crystallinity. The positions of all non-hydrogen atoms except the carbon atoms in **15** were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The refinement for alternative space group for **7** did not yield a good result. The refinements were not well settled in complexes **11a**, **12b** and **19bcf** (0.1 < shift/error < 0.2). All hydrogen atoms were calculated at ideal positions with C–H distances of 0.95 Å).

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See http://www.rsc.org/suppdata/dt/b1/b104811m/ for crystallographic data in CIF or other electronic format.

Summary

In this study, reactions of 1-alkynes or electron-deficient-disubstituted alkynes with the P–O chelate complexes [Cp*MCl(MDMPP-*P*,*O*)] (**1a**: M = Rh; **1b**: M = Ir) and [Cp*MCl(BDMPP-*P*,*O*)] (**2a**: M = Rh; **2b**: M = Ir), derived from reactions of $[Cp^*MCl_2]_2$ (M = Rh, Ir) with (2,6-dimethoxyphenyl)diphenylphosphine or bis(2,6-dimethoxyphenyl)phenylphosphine, in the presence of anions led to the formation of unprecedented complexes; (1) a double insertion of 1-alkyne into an Rh–O σ-bond, (2) a single insertion of HC≡CCOOR into an Rh–O σ-bond accompanying an extraction of CO from an ester, (3) a single insertion of the disubstituted alkyne into Rh–O or Ir–O σ-bonds, (4) a *cis*-insertion of 1-ethynylbenzene derivatives bearing an electron withdrawing substituent into the P–C bond of the phosphine ligand and a transannular addition between a Rh atom and an *ipso*-carbon atom of the phosphine ligand in rhodium and iridium complexes and (5) formation of a carbene complex and a carbonyl complex by a cleavage of a C–C triple bond with H_2O. The manifold reactivity of alkynes for the P–O chelate complexes was found to depend on alkynes, metals and the P–O chelate ligands. We previously reported that the P–O chelate complexes reacted readily with electron-deficient olefins, leading to a novel insertion of the olefin into the C–H bond adjacent to the M–O bond.[14] These results demonstrated that the P–O chelate complexes were able to lead to unprecedented reactions with alkynes and could play a role as useful starting materials in developing activation of small molecules.

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