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PAPER

Facile oxygenation reactions of ruthenium acetylide complex containing substituted olefinic group†

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Reaction of the ruthenium acetylide complex Cp(dppe)RuC≡CCH(OMe)CPh_2–CH_2CH=CMe_2 (**5a**) with oxygen readily gives acetone and the acyl complex **6** in almost quantitative yield. Protonation of **5a** is followed by an elimination of MeOH and a hydroxyl addition at Cα in the presence of water to give the hydroxycarbene complex **7a**. The structures of the acyl complex **6** and the hydroxycarbene complex **7c** are fully characterized by single crystal X-ray diffraction analysis.

Introduction

Oxidation of an organic molecule is a fundamental and practical challenge in chemistry and biology.[1] As an ideal oxidant, O_2 offers appealing prospects.[2] However, because of its mechanistically complicated ground state,[3] O_2 is also a kinetically slow oxidant. Two-electron oxidations of stable organic substrates are impeded by the triplet electronic structure of the ground-state. One-electron oxidations suffer from the disfavored thermodynamics of the initial step.[4] Commonly, O_2 reacts with hydrocarbons by a free radical auotoxidation mechanism. The initial hydroperoxide normally displays unpredictable reactivity under the reaction conditions, and frequently nondiscriminating product formation is observed.[5] Recently a number of papers reported interesting reactions of C≡C triple bond by the participation of O_2. The cleavage of triple bonds in enynols involving gold-catalyzed cascade reactions of enynols with O_2, in which gold was utilized to catalyze independent reactions.[6] The use of O_2 as the sole oxidant[7] for the oxidation of alkynes catalyzed by $PdBr_2$ and $CuBr_2$ provided an access to 1,2-diketones. A report on the Cu-catalyzed oxidative amidation-diketonization reaction of terminal alkynes using O_2 as the oxidant *via* dioxygen activation was also reported.[8] Palladium-catalyzed oxidative alkynylation of alkenes using *tert*-propargylic alcohols *via* a C–C bond cleavage under an oxygen atmosphere afforded the corresponding ene-yne compounds.[9]

In the past decades, enynes have been extensively used in organic synthesis through transition metal-catalyzed reactions because a variety of products can be obtained from fairly simple substrates under mild conditions.[10] Metal-catalyzed cycloisomerizations of enynes have recently been expanded significantly in the synthesis of natural products.[11] Metal-catalyzed cycloisomerization of enynes often leads to various skeletal rearrangements because "non-classical" cations may participate as reaction intermediates.[12] Additionally, the cycloisomerization,[13] metathesis,[14] skeletal rearrangements,[15] and ene reactions[16] of transition metal-catalyzed carbocyclization of enynes[17] reveal a practical strategy for synthesizing five-membered and six-membered alkenes and dienes. With all of these developments, reaction of oxygen with enyne is still rare. Previously, we described the development of ruthenium-mediated isomerizations of 1,5-enynes[18] involving a formal metathesis process of the terminal vinyl group with the C=C of the vinylidene group *via* an unusual mechanism. We continued our study to the skeletal rearrangement of 1,6-propargylic enynes in the $Cp(PPh_3)_2Ru$ system[19] and to the analogous dppe system, in which a new facile oxidation was observed. Compared to PPh_3, dppe ligand is apt to expose the Cα atom of the ruthenium vinylidene or allenylidene complex that leads to much easier attack at Cα by other nucleophiles. As a result, the dppe ligand plays a crucial role in reactions involving Cα. Gimeno and co-workers have reported the steric properties of this very similar metal fragment.[20] These phenomena show that small steric differences of the ancillary ligands in the metal auxiliary are able to completely change the reaction pathway. Herein we report our results on the study of the reaction of a propargyl alcohol with a substituted olefinic group.

Results and discussion

Facile oxygenation

As shown in Scheme 1, the vinylidene complex **2a**, tethering a dimethyl allyl moiety at C4, was prepared as the major product from the reaction of 4,4-diphenylsubstituted propargylic alcohol **1a** with Cp(dppe)RuCl in high yield. We previously reported that the reaction[10] of $Cp(PPh_3)_2RuCl$ with **1a**, in the presence of NH_4PF_6 in methanol at room temperature for 6 h afforded the analogous cationic γ-methoxyvinylidene complex **2a′** and the carbene complex **3a′** in a ratio of 4 : 1, Scheme 1. However, in the Cp(dppe)RuCl system, complex **2a** and the methoxycarbene

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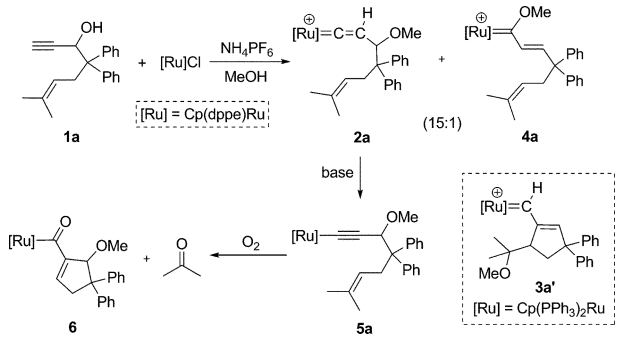


Scheme 1

complex **4a** were obtained in a ratio of 15 : 1 and no cyclization product was observed. To separate **2a** and **4a**, the mixture was treated with excess NEt_3 in CH_2Cl_2 under nitrogen. Only the vinylidene complex **2a** was converted to the corresponding neutral acetylide complex **5a** by deprotonation reaction, and separation of **4a** and **5a** was achieved by chromatography. However, complex **4a** was not obtained in pure form due to the low yield.

Complexes **2a** and **5a** are characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of **2a** in $CDCl_3$, two multiplet peaks at δ 2.16 and 1.82 are assigned to the methylene protons and two singlet peaks at δ 1.37 and 1.19 are assigned to two methyl groups. The ^{31}P NMR spectrum of **2a** exhibits two doublet resonances with an AB pattern at δ 80.21 and 79.87 with $^2J_{pp}$ = 19.6 Hz indicating the presence of a stereogenic carbon center in the vinylidene ligand. The ^{13}C NMR spectrum of **2a** shows the resonance of Cα at δ 337.59 as a triplet peak. In addition, four singlet signals at δ 119.01, 109.84, 77.60 and 36.47 are assigned to ═CH, ═CβH, Cγ and CH_2, respectively.

The ^{1}H NMR spectrum of **5a** shows three singlet peaks at δ 2.63, 1.57 and 1.29 assigned to the protons of the methoxy group and the two methyl groups, respectively. The ^{31}P NMR spectrum of **5a** exhibits two doublet resonances at δ 86.89 and 85.80 with $^2J_{pp}$ = 21.1 Hz. However, our attempts to obtain the ^{13}C spectrum of complex **5a** in the presence of trace oxygen at room temperature failed. As shown in Scheme 1, complex **5a** was converted to the neutral acyl complex **6** and acetone. This transformation can be accelerated by bubbling air through the solution in almost quantitative yield in 10 mins. The terminal three-carbon-unit of **5a** was converted to acetone. For the analogous PPh_3 complex **2a′**, a similar deprotonation yielded **5a′**. Subsequent oxygenation of **5a′** also proceeded to form **6′** in the presence of oxygen, but only in about 29% yield in 4 days and the reaction was accompanied with formation of phosphine oxide $OPPh_3$ in significant amount.

Complex **6** is characterized by NMR spectroscopy as well as single crystal X-ray diffraction analysis. In the ^{13}C NMR spectrum of **6**, the resonance assigned to Cα appears at δ 260.66 as a triplet with $^2J_{CP}$ = 12.9 Hz. The resonances of ═CH, the CH with a neighboring OMe and the methylene groups of the five-membered ring appear at δ 132.65, 88.35 and 43.93, respectively. In the ^{1}H NMR spectrum, resonances of the methylene group appear at δ 3.32 and 2.07 with $^2J_{HH}$ = 16.0 Hz as two broad doublets. The ^{31}P NMR spectrum of **6** exhibits two doublet resonances at δ 97.45 and 90.22 with $^2J_{pp}$ = 21.9 Hz again indicating the presence of a stereogenic carbon center in the five-membered ring. Complex **6** shows an IR ν(C═O) stretching band at 1601 cm^{-1}, within the range for an acyl complex.[21]

Single crystals of complex **6** were obtained from a mixture of CH_2Cl_2–MeOH at room temperature. An ORTEP type view of complex **6** is shown in Fig. 1, with selected bond distances and angles. The complex possesses distorted three-legged piano-stool coordination geometry around the ruthenium center which bound to Cp, dppe and acyl groups. Obviously a C–C bond formation occurred between Cβ and the unsaturated internal carbon of the allylic group, forming a five-membered ring, and formation of a C═O double bond is also observed. The terminal three-carbon-unit of **5a** is no longer on the ligand. The Ru(1)–C(1) bond length in **6** of 2.030(2) Å shows a typical Ru–C single bond for a metal acyl group.[22] The C(2)–C(6) bond length of 1.329(2) Å indicates a C═C bond and the C(1)–C(2)–C(3) bond angle of 120.4(1)° also confirms the sp^2 geometry for C(2).

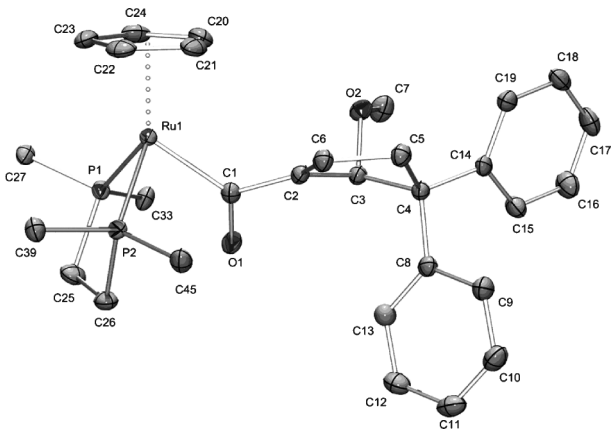


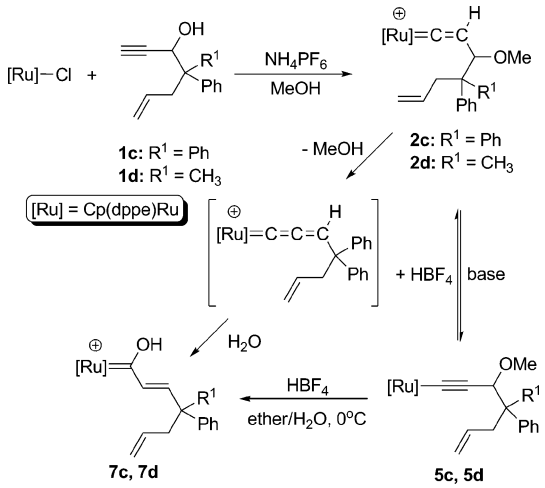
Fig. 1 ORTEP drawing of the ruthenium complex **6**. For clarity, aryl groups of the 1,2-bis(diphenylphosphino)ethane ligand on Ru except the *ipso* carbons are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)–C(1), 2.030(2); C(1)–O(1), 1.244(2); C(1)–C(2), 1.510(2); C(3)–O(2), 1.434(2); C(7)–O(2), 1.419(2); C(2)–C(6), 1.329(2); C(2)–C(3), 1.514(2); C(5)–C(6), 1.509(2); Ru(1)–C(1)–O(1), 126.5(1); Ru(1)–C(1)–C(2), 121.1(1); O(1)–C(1)–C(2), 112.4(1); C(1)–C(2)–C(3), 120.4(1); C(2)–C(3)–C(4), 103.0(1); C(3)–C(4)–C(5), 101.2(1); C(4)–C(5)–C(6), 102.4(1); C(6)–C(2)–C(3), 109.6(1).

To study the effect of methyl groups on the olefinic unit, we synthesized the analogous complex **5b**, having only one methyl group on the terminal carbon of the tethering allyl group from a *trans* and *cis* mixture of 4,4-diphenyloct-6-en-1-yn-3-ol (**1b**). Complex **5b** consists of a mixture of *trans* and *cis* isomers of the terminal methyl group. The similar oxygenation reaction of **5b** was also completed in 1 h, and the same acyl complex **6** and acetaldehyde were observed spectroscopically. No reaction was observed when complex **5a** was treated with ethyl vinyl ether or another activated olefin containing an electron-withdrawing group, under nitrogen or even under reflux.

Hydroxycarbene complex

Using the same procedure as that used for the preparation of **5a**, two other acetylide complexes **5c** and **5d** containing 4,4-disubstituted acetylide ligand each tethering a non-substituted terminal vinyl group were obtained from **1c** and **1d**, respectively,

Scheme 2. Facile oxygenation, observed in **5a** and **5b**, was not found for **5c** and **5d**. However, in the presence of water, treatment of the acetylide complexes **5a**, **5c** and **5d** with HBF_4 in ether at 0 °C generated the corresponding light orange ruthenium hydroxycarbene complexes **7a**, **7c** and **7d**, respectively, all as solid precipitates in high yield. Complexes **7a**, **7c** and **7d** were characterized by NMR data and additionally complex **7c** was characterized by a single crystal X-ray diffraction analysis.



Scheme 2

The ^{31}P NMR spectrum of **7c** exhibits a singlet peak at δ 95.32. No methoxy resonance is found in the ^{1}H NMR spectrum of complex **7c**. The ^{1}H NMR spectrum of **7c** displays two doublet peaks at δ 6.11 and 5.68 with $^{3}J_{HH} = 15.5$ Hz assigned to Cγ–H and Cβ–H, respectively, indicating a *trans* configuration of the double bond. The doublet peak at δ 2.74 is assigned to the methylene protons. The ^{13}C NMR spectrum of **7c** shows a triplet resonance at δ 285.44 assigned to Ru=Cα.

Recrystallization of **7c** from CH_2Cl_2–hexane at room temperature for 2 days afforded light orange single crystals suitable for X-ray diffraction analysis. The solid-state molecular structure of **7c** has been determined. An ORTEP diagram is shown in Fig. 2. The short Ru(1)–C(1) metal–carbon distance of 1.952(4) Å is a metal carbon double bond. Similar bond lengths have been reported in other related ruthenium carbene complexes.[23] The bond length of C(1)–O(1) of 1.343(4) Å is considered as a C–O single-bond. Gladfelter and co-workers have found that the C–O distance in $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(OH)C_2(CO_2Me)_2]$ complex, a dimer containing conjugate system, is 1.39(3) Å.[24] The bond lengths of C_{sp^2}–O in organic compounds are commonly in the range of 1.29(3)–1.40(7) Å; the shortened single bond is 1.29(3) Å in C=C–C(=O)–OH and the elongated bond is 1.40(7) Å in C–C(=O)–O–C=C. However, the bond lengths of C_{sp^2}=O are around 1.18(7)–1.25(4) Å indicating a carbonyl compound.[25] Complex **7c** is thus a hydroxycarbene complex. Transition metal hydroxycarbene complexes are known to be synthesized by direct protonation of a metal acyl complex.[26] Other hydroxycarbene complexes, such as $[(dppp)(CO)_3Mn{=}C(OH)\text{-}CH_3]$[27] and $OsCl_2[{=}C(OH)C_3H_3(Ph\text{-}2)_2](CO)(PPh_3)_2$[28] have been reported.

When the protonation reaction of **5c** was carried out with a dilute solution of HBF_4/ether/H_2O at 0 °C to slow down the reaction rate in an NMR tube, both ^{1}H resonances of **2c** and

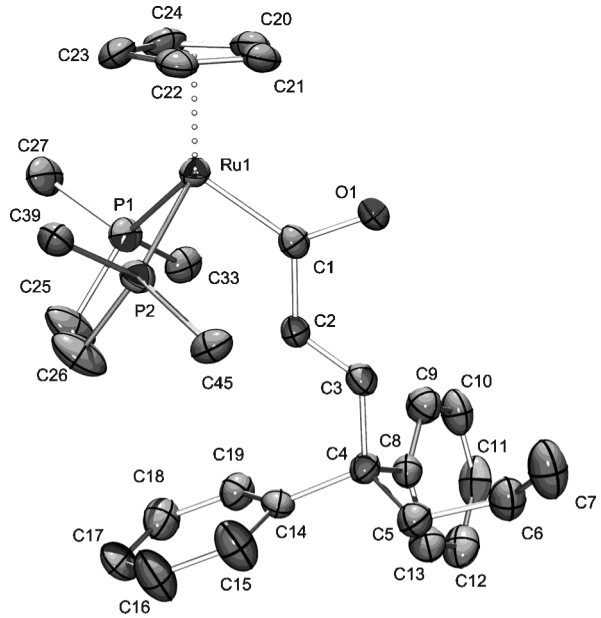


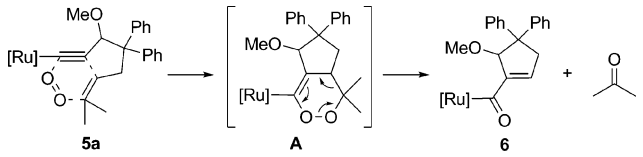
Fig. 2 ORTEP drawing of the ruthenium complex **7c**. For clarity, aryl groups of the 1,2-bis(diphenylphosphino)ethane ligand on Ru except the *ipso* carbons are omitted (thermal ellipsoid is set at the 50% probability level). Selected bond distances (Å) and angles (deg): Ru(1)–C(1), 1.950(3); C(1)–C(2), 1.472(4); C(2)–C(3), 1.320(5); C(5)–C(6), 1.496(5); C(6)–C(7), 1.291(6); C(1)–O(1), 1.345(4); Ru(1)–C(1)–O(1), 125.2(2); Ru(1)–C(1)–C(2), 127.3(2); C(1)–C(2)–C(3), 126.1(3); C(2)–C(3)–C(4), 127.5(3); C(4)–C(5)–C(6), 115.1(3); C(5)–C(6)–C(7), 124.3(4).

7c in the NMR spectrum were observed and the resonance of **2c** gradually disappeared. This implies that the reaction of **5c** to give **7c** could proceed *via* the vinylidene complex **2c**. Indeed, direct treatment of **2c** with HBF_4, in the presence of water, afforded complex **7c**. The elimination of MeOH, which gives the allenylidene intermediate in the presence of acid, is proposed because of the basicity of the characteristic methoxy group on the vinylidene complex **2c**. A similar MeOH elimination process has been reported by Werner and co-workers.[29] The dehydration of hydroxyvinylidene derivatives have been promoted by catalytic quantities of acid.[29] After elimination of MeOH, the electrophilic character of Cα in the allenylidene intermediate favors the addition of water at Cα to give the hydroxycarbene complex **7c**, Scheme 2.[30,31]

Nevertheless, the protonation of the acetylide complex **5c′** containing PPh_3 ligand with HBF_4 in the presence of water only yielded the vinylidene product **2c′** like many other acetylide complexes in the literature.[32] When excess HBF_4 was added to the ether solution, the allenylidene complex was observed. However, no hydroxycarbene complex could be obtained. The steric effect of the PPh_3 ligand could be significant in blocking the Cα atom.

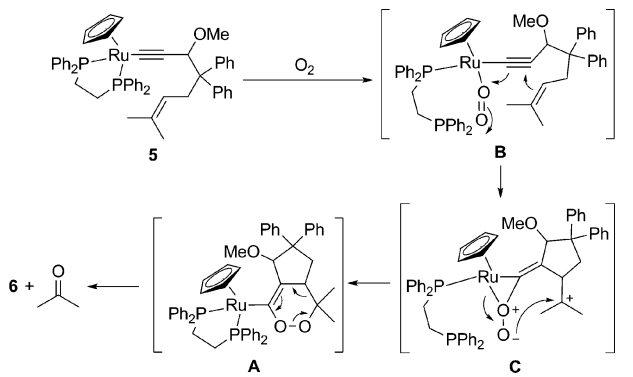
Possible mechanism

A rational and simplified mechanism for the formation of **6** is proposed in Scheme 3. Molecular oxygen readily reacts possibly *via* a [2+2+2] cyclization with the 1,6-enyne ligand of complex **5a**. A C–C bond formation between Cβ and the unsaturated internal carbon of the allylic group gives the intermediate **A**.



Scheme 3

This process presumably requires photo-activation of oxygen to a singlet state. A number of ruthenium complexes have been used as sensitizers in photo reactions involving oxygen.[33] Therefore, we carried out the reaction in the dark and found no effect on the formation of **6**. Thus the ruthenium metal center may serve to assist this [2+2+2] cyclization possibly by providing a coordination site leading to **B** as shown in Scheme 4. Then the intermediate **B** transforms, *via* **C** and **A**, to the acyl product **6** and acetone. In the $Cp(PPh_3)_2Ru$ system, low yield of **6′** was accompanied with substantial formation of $OPPh_3$. This indicates that phosphine dissociation, which was caused by the steric effect between phosphine ligands and the two phenyl groups in the enyne chain, may indeed occur in this oxygenation reaction. The studies of Jugé demonstrated that the oxidation of olefin with molecular oxygen, promoted by a transition metal catalyst and thiophenol, resulted in a C=C bond cleavage giving the corresponding carbonyl derivatives.[34] Jones and co-workers reported that 1,4-diphenyl-2-benzopyran-3-one *endo*-peroxides was easily accessible through singlet oxygenation of α-pyrone.[35] In addition, the studies of Schuster demonstrated that thermal decomposition of 1,4-diphenyl-2-benzopyran-3-one *endo*-peroxide led to *o*-xylylene peroxide, which subsequently rearranged to give *o*-dibenzoylbenzene.[36] The decarboxylation preserved the peroxide linkage in the form of the 1,2-dioxin moiety in the *o*-xylylene peroxide. The 1,4-cycloaddition between molecular oxygen and conjugated dienes was proposed in the photooxygenation of α-pyrone. These reactions had been known for years, and oxygen in a singlet excited state is considered as the active species in these reactions.[37] This concerted Diels–Alder-like mechanism *i.e.* a two-step mechanism involving an intermediate, which rearranges to give the *endo*-peroxide, have been proposed, but the required reaction time is usually long. In our enyne case, oxygen addition to **5a** very likely proceeds *via* coordination to the metal giving the *endo*-peroxide intermediate **A** *via* **B** and **C**, then eliminates acetone to yield the acyl product **6**.



Scheme 4

Conclusions

The novel oxygenation reaction of the ruthenium 1,2-bis(diphenylphosphino)ethane acetylide complexes containing 4,4-disubstituted-1,6-enynes is reported. With the presence of one or two methyl groups at the terminal carbon of the tethering vinyl group, the acetylide complexes **5a**, **5b** and **5a′** display unexpected facile reaction with oxygen. The reaction results in a C–C bond formation between Cβ and the central olefinic carbon of the allylic group followed by the elimination of acetone to give the acyl complex **6** and **6′**. Protonation of the acetylide complexes **5a**, **5c** and **5d** is followed by a MeOH elimination. Then addition of a hydroxyl group, in the presence of H_2O, at Cα yields the hydroxy-carbene complexes **7a**, **7c** and **7d**, respectively. Protonation of the analogous triphenylphosphine acetylide complex with HBF_4 yields the vinylidene product only, most likely owing to the steric effect of the phosphine ligand blocking Cα for the addition of a hydroxyl group.

Experimental

General procedures

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The ruthenium complex Cp(dppe)RuCl[38] and compounds **1a–1d**[39] were prepared by following the method reported in the literature. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded using a LCQ Advantage (ESI) and JEOL SX-102A (FAB). X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. NMR spectra were recorded on Bruker Avance-400 and DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as a standard.

Reaction of 1a and 1b with [Ru]Cl. A typical experimental procedure for the reaction of [Ru]Cl with enyne is described below. To a Schlenk flask containing Cp(dppe)RuCl (0.10 g, 0.24 mmol), NH_4PF_6 (0.10 g, 0.61 mmol) and 1,6-enyne **1a** (0.104 g, 0.36 mmol), 20 mL of MeOH was added at room temperature. The resulting solution was stirred at room temperature for four days and MeOH was then removed under vacuum. The product was dissolved in CH_2Cl_2 and the mixture was filtered through Celite to remove the insoluble precipitates. The volatiles of the filtrate were removed under vacuum and the solid residue was extracted with a small volume of dichloromethane followed by re-precipitation by addition of 60 mL of diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether and dried under vacuum to give a mixture of the vinylidene complex **2a** and the methoxycarbene complex **4a** (0.11 g, total yield 73%). The ratio of complexes **2a** to **4a** is about 15 : 1. Complex **2a** in the mixture is used for the next step without further purification. Spectroscopic data for **2a**: ^{1}H NMR ($CDCl_3$): δ 7.45–6.53 (m, 30H, Ph); 5.36 (s, 5H, Cp); 4.67 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C*H*=CMe_2); 4.04 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Cγ–H); 3.25–2.94 (m, 5H, Cβ–H and dppe); 2.92 (s, 3H, OMe); 2.58, 2.16 (m, 2H, CH_2); 1.37, 1.19 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 15 °C): δ 337.59 (t, $^2J_{PC}$ = 16.6 Hz,

Cα); 148.41–125.83 (Ph); 119.01 (*C*H═CMe$_2$); 109.84 (Cβ); 92.39 (Cp); 77.60 (Cγ); 55.98 (OMe); 55.83 (CPh$_2$); 36.47 (CH$_2$); 28.10–27.59 (m, dppe). ^{31}P NMR (CDCl$_3$): δ 80.21, 79.87 (two d, $^2J_{pp}$ = 19.6 Hz, dppe). Pure complex **2a** was not obtained. Spectroscopic data for **4a**: ^{31}P NMR (CDCl$_3$): δ 91.47 (s, dppe). The synthesis of a mixture of **2b** and **4b** (also in a ratio of 15 : 1 with total yield of 71%) followed the same procedure. Spectroscopic data for **2b**: ^{1}H NMR (CDCl$_3$): δ 7.99–6.65 (m, 30H, Ph); 5.36 (s, 5H, Cp); 5.11 (m, 1H, C*H*═CHMe); 4.84 (m, 1H, CH═C*H*Me); 4.01 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Cγ–H); 3.08–2.73 (m, 5H, Cβ–H and dppe); 2.92 (s, 3H, OMe); 2.62, 2.23 (m, 2H, CH$_2$); 1.47 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 15 °C): δ 337.49 (t, $^2J_{PC}$ = 15.8 Hz, Cα); 148.20–125.90 (Ph); 129.45 (*C*H═CHMe); 109.78 (Cβ); 92.40 (Cp); 80.32 (Cγ); 55.96 (OMe); 55.73 (CPh$_2$); 39.56 (CH$_2$); 28.17–27.64 (m, dppe), 18.09 (CH$_3$). ^{31}P NMR (CDCl$_3$): δ 80.23, 79.98 (two d, $^2J_{pp}$ = 19.8 Hz, dppe). No attempt was made to purify complex **2b**. Spectroscopic data for **4b**: ^{31}P NMR (CDCl$_3$): δ 91.38 (s, dppe).

Synthesis of 5a and 5b. To a solution of the mixture of **2a** and **4a** (0.11 g, *ca.* 0.12 mmol) obtained directly from **1a** in dichloromethane (20 mL) in a 150 mL round-bottom flask, excess triethylamine (2 mL) was added at room temperature and the mixture was stirred overnight. Then, volatiles were removed *in vacuo* and ether (5 mL × 3) was added to extract the residue, which was filtered through Celite and the solvent of the filtrate was removed under vacuum to give the light yellow acetylide complex **5a** (0.06 g, 54% yield). Spectroscopic data for **5a**: ^{1}H NMR (CDCl$_3$): δ 7.82–6.56 (m, 30H, Ph); 4.76 (t, 1H, $^3J_{HH}$ = 6.6 Hz, C*H*CMe$_2$); 4.20 (s, 1H, *H*COMe); 4.70 (s, 5H, Cp); 2.72 (m, 2H, CH$_2$); 2.63 (s, 3H, OMe); 1.56, 1.26 (two s, 6H, CH$_3$). ^{31}P NMR (CDCl$_3$): δ 86.89, 85.80 (two d, $^2J_{pp}$ = 21.1 Hz, dppe). Anal. Calcd. For C$_{53}$H$_{52}$OP$_2$Ru: C, 73.34; H, 6.04. Found: C, 73.07; H, 6.01. The synthesis of **5b** in 68% yield followed the same procedure. Spectroscopic data for **5b**: ^{1}H NMR (CDCl$_3$): δ 7.87–7.09 (m, 30H, Ph); 5.18–5.04 (m, 2H, ═CH); 4.76 (s, 5H, Cp); 4.32 (s, 1H, *H*COMe); 2.69 (s, 3H, OMe); 2.64 (m, 2H, CH$_2$); 1.57 (d, $^2J_{pp}$ = 5.9 Hz, 3H, CH$_3$). ^{31}P NMR (CDCl$_3$): δ 86.95, 85.55 (two d, $^2J_{pp}$ = 21.7 Hz, dppe). ^{13}C NMR (CDCl$_3$): δ 139.14–125.31 (Ph), 135.03 (*C*H═CHMe), 125.43 (CH═*C*HMe), 105.69 (Cβ), 105.83 (t, $^2J_{PC}$ = 25.0 Hz, Cα), 82.64 (Cp), 78.29 (Cγ), 56.01 (CPh$_2$), 54.97 (OMe), 30.12 (CH$_2$), 18.26 (CH$_3$). MS ESI *m*/*z*: 855.0 (M+1)$^+$.

Synthesis of 5a′. To a Schlenk flask containing the mixture of **2a′** and **4a′** (in a ratio of 4 : 1, 0.10 g, 0.09 mmol), excess NaOMe (0.10 g, 2.27 mmol) in 30 mL MeOH was added at room temperature. The resulting solution was stirred at room temperature for 15 mins and the solvent was then removed under vacuum. The product was dissolved in CH$_2$Cl$_2$ and the mixture was filtered through Celite to remove the insoluble precipitates. Then the solvent of the filtrate was removed under vacuum and the solid residue was extracted with diethyl ether to yield the light yellow acetylide complex **5a′** (0.06 g, 89% yield). Spectroscopic data for **5a′**: ^{1}H NMR (CDCl$_3$): δ 7.41–7.06 (m, 40H, Ph); 5.06 (t, 1H, $^3J_{HH}$ = 5.8 Hz, C*H*CMe$_2$); 4.69 (s, 1H, *H*COMe); 4.14 (s, 5H, Cp); 3.16 and 2.99 (two m, 2H, CH$_2$); 2.96 (s, 3H, OMe); 1.58, 1.26 (two s, 6H, CH$_3$). ^{31}P NMR (CDCl$_3$): δ54.83, 54.57 (two d, $^2J_{pp}$ = 37.3 Hz).^{13}C NMR (CDCl$_3$, 5 °C): δ 160.59–127.04 (Ph), 133.13 (*C*H═CMe$_2$), 121.05 (CH═*C*Me$_2$), 108.50 (Cβ), 104.56 (t, $^2J_{PC}$ = 23.3 Hz, Cα), 84.45 (Cp), 78.57 (Cγ), 56.87 (CPh$_2$), 56.15 (OMe), 26.01 (CH$_2$), 25.80, 17.76 (two singlet, CH═C*Me$_2$). MS ESI *m*/*z*: 995.3 (M+1)$^+$. Anal. Calcd. For C$_{63}$H$_{58}$OP$_2$Ru: C, 76.11; H, 5.88. Found: C, 75.97; H, 6.01.

Synthesis of 6. Oxygen gas was gently bubbled through a solution of the acetylide complex **5a** (0.06 g, 0.07 mmol) in CDCl$_3$ at room temperature for 10 min. The acetylide complex **5a** was transformed into the acyl complex **6** in almost quantitative yield. The solvent was removed *in vacuo* and the neutral ruthenium acyl complex **6** (0.059 g, 100% yield) was obtained. Treatment of the acetylide complex **5b** with oxygen gas in CDCl$_3$ also generated complex **6**. Spectroscopic data for **6**: ^{1}H NMR (CDCl$_3$): δ 7.91–6.66 (m, 30H, Ph); 4.90 (s, 1H, CH); 4.82 (s, 5H, Cp); 4.41 (t, $^2J_{HH}$ = 2.4 Hz, 1H, C═C*H*); 3.32, 2.07 (two d, $^3J_{HH}$ = 16.0 Hz, 2H, CH$_2$); 3.19 (s, 3H, OMe); 3.07–2.88, 2.43–2.26 (m, 4H, dppe). ^{13}C NMR (C$_6$D$_6$): δ 260.66 (t, $^2J_{PC}$ = 12.9 Hz, Cα); 160.03–125.16 (Ph); 132.65 (C═*C*H); 88.35 (CH); 85.94 (Cp); 59.65 (CPh$_2$); 58.71 (OMe); 43.93 (CH$_2$); 27.01, 24.23 (two m, CH$_2$ of dppe). ^{31}P NMR (CDCl$_3$): δ 97.45, 90.22 (two d, $^2J_{pp}$ = 21.9 Hz, dppe). MS ESI *m*/*z*: 843.2 (M+1)$^+$. Anal. Calcd for C$_{50}$H$_{46}$O$_2$P$_2$Ru: C, 71.33; H, 5.51. Found: C, 71.27; H: 5.46.

Synthesis of 6′. The solution of complex **5a′** (70 mg, 0.07 mmol) in CDCl3 was exposed to air at room temperature for 2 days. The reaction was monitored by ^{31}P NMR spectroscopy. At the end of the reaction complex **6′** and OPPh$_3$ in a ratio of 1 : 2.1 were observed. Then the solvent was removed under vacuum and the residue dissolved in ether. The solution was passed through a column packed with neutral aluminium oxide using ether as the eluent. A yellow band was collected to yield the neutral acyl complex **6′** (0.02 g, 29% yield). Spectroscopic data for **6′**: ^{1}H NMR (CDCl$_3$): δ 7.42–7.06 (m, 40H, Ph); 5.22 (br, s, 1H, C═C*H*); 5.18 (s, 1H, CH); 4.39 (s, 5H, Cp); 3.49, 2.43 (two d, $^3J_{HH}$ = 16.4 Hz, 2H, CH$_2$); 3.07 (s, 3H, OMe). ^{31}P NMR (CDCl$_3$): δ 52.44, 51.33 (two d, $^2J_{pp}$ = 35.4 Hz, PPh$_3$).

Reactions of 1c–1d with [Ru]Cl. To a Schlenk flask containing Cp(dppe)RuCl (0.10 g, 0.24 mmol), NH$_4$PF$_6$ (0.10 g, 0.61 mmol) and 1,6-enyne **1c** (0.095 g, 0.36 mmol), 20 mL of MeOH was added at room temperature. The mixture was stirred under nitrogen at room temperature for 4 days and MeOH was then removed under vacuum. The product was dissolved in CH$_2$Cl$_2$ and the mixture was filtered through Celite. The solvent was then removed under vacuum, and the solid residue was extracted with a small volume of dichloromethane followed by re-precipitation by a 60 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether and dried under vacuum. The final product can be obtained as a red powder **2c** (0.12 g, 85.6%). Spectroscopic data for **2c**: ^{1}H NMR (CDCl$_3$): δ 7.65–6.68 (m, 30H, Ph); 5.37 (s, 5H, Cp); 5.13 (m, 1H, C*H*═CH$_2$); 4.78 (d, $^3J_{HH}$ = 9.8 Hz, 1H, *cis* ═CH$_2$); 4.76 (d, $^3J_{HH}$ = 16.9 Hz, 1H, *trans* ═CH$_2$); 4.04 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Cβ–H); 3.09, 2.94 (m, 4H, dppe); 3.07 (s, 3H, OMe); 2.68, 2.34 (m, 2H, CH$_2$). ^{13}C NMR (CDCl$_3$, 15 °C): δ 337.54 (t, $^2J_{PC}$ = 15.9 Hz, Cα); 145.24–126.07 (Ph); 134.01 (*C*H═CH$_2$); 117.68 (CH═*C*H$_2$); 109.64 (Cβ); 92.45 (Cp); 80.33 (Cγ); 55.93 (OMe); 42.39 (CH$_2$); 28.15–27.77 (m, dppe). ^{31}P NMR (CDCl$_3$): δ 80.12, 79.79 (two d, $^2J_{pp}$ = 19.6 Hz, dppe); Pure complex **2c** was not obtained. The synthesis of **2d** followed the same procedure. Spectroscopic data for **2d**: (ratio of

isomers about 1 : 1) ^{1}H NMR (CD_3COCD_3): δ 8.52–6.63 (m, 25H, Ph); 5.93 and 5.24 (two m, 1H, C*H*=CH_2); 5.73 and 5.60 (two s, 5H, Cp); 4.84 (d, $^3J_{HH}$ = 17.4 Hz, 1H, *trans* =CH_2); 4.77 (d, $^3J_{HH}$ = 10.2 Hz, 1H, *cis* =CH_2); 3.17 and 2.92 (two s, 3H, OMe); 3.00–2.79 (m, 4H, dppe); 2.32–2.11 (m, 2H, CH_2); 0.86 and 0.81 (two s, 3H, CH_3). ^{13}C NMR (CD_3COCD_3, 15 °C): δ 338.72 (t, $^2J_{PC}$ = 16.2 Hz), 338.19 (t, $^2J_{PC}$ = 16.0 Hz, Cα); 144.29–126.76 (Ph); 134.29 and 134.21 (*C*H=CH_2); 117.81, 117.52 (CH=*C*H_2); 109.66, 109.61 (Cβ); 93.32 (Cp); 81.08, 80.95 (Cγ); 56.56, 56.55 (OMe); 42.39 (CH_2); 28.36–27.24 (m, dppe). ^{31}P NMR (CD_3COCD_3): δ 79.83, 79.20 (two d, $^2J_{pp}$ = 20.6 Hz, dppe); 79.29, 78.98 (two d, $^2J_{pp}$ = 20.5 Hz, dppe). Pure complex **2d** was not obtained.

Syntheses of 5c, 5d and 5a′. Complex **2c** (0.12 g, 0.14 mmol) was treated with excess K_2CO_3 (0.19 g, *ca.* 10 equiv.) in methanol (20 mL). The mixture was stirred in air at room temperature for 10 min and MeOH was removed under vacuum. The residue was dissolved in ether, then filtered through Celite and the solvent was removed under vacuum to give the yellow acetylide complex **5c** (0.11 g, 90% yield). Spectroscopic data for **5c**: ^{1}H NMR (C_6D_6): δ 7.78–6.97 (m, 30H, Ph), 5.36 (m, 1H, C*H*=CH_2), 4.77 (d, $^3J_{HH}$ = 9.9 Hz, 1H, *cis* =CH_2), 4.74 (d, $^3J_{HH}$ = 18.6 Hz, 1H, *trans* =CH_2), 4.70 (s, 5H, Cp), 4.25 (s, 1H, CH), 2.68 (d, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2), 2.63 (s, 3H, OMe), 2.37–2.06 (m, 4H, dppe). ^{13}C NMR (C_6D_6): δ 147.19–125.39 (Ph), 136.89 (*C*H=CH_2), 116.68 (CH=*C*H_2), 105.49 (Cβ), 106.14 (t, $^2J_{PC}$ = 25.1 Hz, Cα), 82.63 (Cp), 55.67 (OMe), 54.95 (CPh_2), 51.54 (Cγ), 43.57 (CH_2), 28.75–28.37, 27.72–27.36 (two m, dppe). ^{31}P NMR (C_6D_6): δ 86.87, 85.55 (two d, $^2J_{pp}$ = 22.0 Hz, dppe). MS ESI *m*/*z*: 841.2 (M+1)$^+$. Anal. Calcd. For $C_{51}H_{48}OP_2Ru$: C, 72.93; H, 5.76. Found: C, 72.96; H, 5.78. The synthesis of **5d** followed the same procedure. Spectroscopic data for **5d**: (ratio of isomers about 1 : 1) ^{1}H NMR (C_6D_6): δ 7.87–6.78 (m, 25H, Ph), 5.70 (m, 1H, C*H*=CH_2), 5.09 (d, $^3J_{HH}$ = 15.0 Hz, 1H, *trans* =CH_2), 4.98 (d, $^3J_{HH}$ = 10.0 Hz, 1H, *cis* =CH_2), 4.83, 4.77 (two s, 5H, Cp), 3.99 (d, $^3J_{HH}$ = 10.6 Hz, 1H, CH), 3.25, 3.03 (two s, 3H, OMe), 2.75–2.55 (m, 2H, CH_2), 2.54–2.52, 2.30–2.06 (two m, 4H, dppe), 1.42, 1.40 (two d, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 147.19–125.39 (Ph), 136.87, 136.80 (*C*H=CH_2), 116.36, 116.26 (CH=*C*H_2), 106.62, 106.52 (Cβ), 105.02, 104.52 (two t, $^2J_{PC}$ = 25.8 Hz, Cα), 82.67, 82.56 (Cp), 55.68, 55.61 (OMe), 46.56, 46.55 (Cγ), 43.89, 43.88 (CH_2), 28.57–27.75 (m, dppe). ^{31}P NMR ($CDCl_3$): δ 87.28, 86.91 (two d, $^2J_{pp}$ = 21.2 Hz, dppe), 87.01, 86.78 (two d, $^2J_{pp}$ = 21.7 Hz, dppe). MS ESI *m*/*z*: 779.2 (M+1)$^+$. Anal. Calcd. For $C_{46}H_{46}OP_2Ru$: C, 71.03; H, 5.96. Found: C, 70.95; H, 5.88. The synthesis of **5a′** followed the same procedure. Spectroscopic data for **5a′**:^{1}H NMR (C_6D_6): δ 7.81–6.89 (m, 40H, Ph), 5.94 (m, 1H, C*H*=CH_2), 5.17 (d, $^3J_{HH}$ = 17.2 Hz, 1H, *trans* =CH_2), 5.06 (s, 1H, CH), 5.02 (d, $^3J_{HH}$ = 10.2 Hz, 1H, *cis* =CH_2), 4.36 (s, 5H, Cp), 3.52 (d, $^3J_{HH}$ = 6.9 Hz, 2H, CH_2), 3.24 (s, 3H, OMe). ^{13}C NMR (C_6D_6): δ 147.17–125.80 (Ph), 136.79 (*C*H=CH_2), 117.20 (CH=*C*H_2), 109.37 (Cβ), 104.58 (t, $^2J_{PC}$ = 23.75 Hz, Cα), 85.73 (Cp), 78.85 (CPh_2), 56.36 (OMe), 56.27 (Cγ), 44.41 (CH_2). ^{31}P NMR (C_6D_6): δ 51.29, 50.92 (two d, $^2J_{pp}$ = 37.40 Hz, PPh_3). MS ESI *m*/*z*: 967.3 (M+1)$^+$. Anal. Calcd. For $C_{61}H_{54}OP_2Ru$: C, 75.84; H, 5.63. Found: C, 75.92; H, 5.86.

Syntheses of 7a, 7c and 7d. A Schlenk flask was charged with the acetylide complex **5a** (0.11 g, 0.13 mmol) in ether (20 mL) after atmosphere was replaced with nitrogen. HBF_4 (54% in ether, 0.15 mmol), diluted by ether (2 mL), was added drop wise to the solution at 0 °C. Light yellow precipitate formed immediately, but addition of HBF_4 was continued until no further solid formed. The precipitate was filtered and washed with ether (5 mL × 2) and dried under vacuum to give the final product **7a** (0.090 g, in 83% yield) as light yellow powder. The syntheses of **7c** and **7d** followed the same procedure. Spectroscopic data for **7a**: ^{1}H NMR ($CDCl_3$): δ 11.45 (br, 1H, OH); 7.60–6.73 (m, 25H, Ph); 6.27 (d, $^3J_{HH}$ = 15.5 Hz, 1H, Cγ–H); 5.63 (d, $^3J_{HH}$ = 15.5 Hz, 1H, Cβ–H); 5.37 (m, 1H, C*H*=CH_2); 4.76 (s, 5H, Cp); 1.41, 1.26 (s, 6H, CH_3). ^{31}P NMR ($CDCl_3$): δ 95.22 (s, dppe). Spectroscopic data for **7c**: ^{1}H NMR ($CDCl_3$): δ 11.36 (br, 1H, OH); 7.68–6.80 (m, 30H, Ph); 6.11, (d, $^3J_{HH}$ = 15.5 Hz, 1H, CγH); 5.68 (d, $^3J_{HH}$ = 15.5 Hz, 1H, CβH); 5.27 (m, 1H, C*H*=CH_2); 4.94 (d, $^3J_{HH}$ = 19.5 Hz, 1H, *trans* =CH_2); 4.93 (d, $^3J_{HH}$ = 11.2 Hz, 1H, *cis* =CH_2); 4.76 (s, 5H, Cp); 2.96, 2.60 (two m, 4H, dppe); 2.74 (d, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 285.37 (t, $^2J_{PC}$ = 11.4 Hz, Cα); 144.61 (Cβ); 138.84 (Cγ); 134.00 (*C*H=CH_2); 133.92–126.47 (Ph); 118.81 (CH=*C*H_2); 90.55 (Cp); 52.82 (CPh_2); 42.82 (CH_2); 28.95 (m, $^2J_{PC}$ = 22.7 Hz, dppe). ^{31}P NMR ($CDCl_3$): δ 95.27 (s, dppe). MS ESI *m*/*z*: 827.2 (M+). Anal. Calcd. For $C_{50}H_{47}OP_2Ru$: C, 72.62; H, 5.73. Found: C, 72.70; H, 5.78. Spectroscopic data for **7d**: ^{1}H NMR ($CDCl_3$): δ 11.26 (br, 1H, OH); 7.75–6.82 (m, 25H, Ph); 6.10 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CγH); 5.59 (d, $^3J_{HH}$ = 16.0 Hz, 1H, CβH); 5.37 (m, 1H, C*H*=CH_2); 4.99 (d, $^3J_{HH}$ = 15.6 Hz, 1H, *trans* =CH_2); 4.96 (d, $^3J_{HH}$ = 9.0 Hz, 1H, *cis* =CH_2); 4.85 (s, 5H, Cp); 3.12, 2.60 (two m, 4H, dppe); 2.44 and 2.30 (two m, 2H, CH_2); 1.22 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): δ 94.81, 94.60 (two d, $^2J_{pp}$ = 19.4 Hz, dppe). MS ESI *m*/*z*: 765.2 (M+). Anal. Calcd. For $C_{45}H_{45}OP_2Ru$: C, 70.66; H, 5.93. Found: C, 70.58; H, 5.82.

X-ray structure determination of 6 and 7c. A single crystal of **6** suitable for an X-ray diffraction study was glued to a glass fiber and mounted on a Nonius Kappa CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube molybdenum Kα radiation (T = 295 K). The exposure time was 5 s per frame. Multiscan absorption correction was applied, and decay was negligible. Data were processed, and the structures were solved and refined by the SHELXTL program.[40] The structure was solved

Table 1 Crystal Data and Refinement Parameters for Complexes **6** and **7c**

	6	**7c**
Formula	$C_{50}H_{46}O_2P_2Ru$	$C_{101}H_{94}O_2P_4Ru_2B_2F_8{\cdot}CH_2Cl_2$
Formula weight	841.88	998.62
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	9.7453(2)	10.0082(3)
b/Å	9.8887(2)	20.6549(5)
c/Å	21.9565(3)	21.9508(6)
α (°)	102.050(1)	90
β (°)	96.640(1)	95.564(2)
γ (°)	101.361(2)	90
V/Å^3	2001.44(6)	4516.3(2)
Z	2	2
Reflns collected	46602	20880
Indep reflns (*R*int)	9189(0.0285)	10056 (0.0358)
Goodness-of-fit on F^2	0.944	0.817
R_1, wR_2 [$I > 2\sigma(I)$]	0.0228/0.0567	0.0427/0.1034
R_1, wR_2 (all data)	0.0282/0.0585	0.0843/0.1132

using direct methods and confirmed by Patterson methods refined on intensities of data to give R1 and wR2 for unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times those for the atoms to which the hydrogens are attached and 1.5 times those for the methyl hydrogen atoms. Solid-state structure determinations were similarly carried out for **7c**. Table 1 gives parameters of the crystal data and refinement for complexes **6 (**CCDC 798981) and **7c**. (CCDC 798980). For **7c**, a model with a CH_2Cl_2 hemisolvate with a half-occupied solvent site (disordered over a centre of inversion) was used to the exceptionally large thermal ellipsoids of the CH_2Cl_2 moiety.

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