Conditioned P−CH$_2$ Bond Cleavage of a μ-DPPM Ligand in a Cationic Diruthenium System

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Thermal reactions of [Ru$_2$(CO)$_4$(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ ([**1**]$^+$) with an excess amount of neutral two-electron nucleophiles in MeCN have been studied. The P−CH$_2$ bond of one coordinated DPPM ligand can be cleaved, depending on the choice of the nucleophiles used. Reactions of [**1**]$^+$ with MeCN and phosphite P(OMe)$_3$ afford only substituted products [Ru$_2$(CO)$_2$L$_2$(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ (L = MeCN ([**2a**]$^+$), P(OMe)$_3$ ([**2b**]$^+$)) via intermediates [Ru$_2$(CO)$_3$L(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ (L = MeCN ([**3a**]$^+$), P(OMe)$_3$ ([**3b**]$^+$)). Compounds [**2a**]$^+$ and [**3a**]$^+$ can be prepared alternatively from decarbonylation reaction of [**1**]$^+$ with a suitable amount of Me$_3$NO in MeCN at ambient temperature, and the structure of [**3a**][BPh$_4$] has been determined by X-ray diffraction. Reactions of [**1**]$^+$ with phosphines (PR$_3$) PPh$_3$, PPh$_2$Me, and PEt$_3$, however, yield unexpected products, [Ru$_2$(CO)$_2$(PR$_3$)$_2$(μ-O$_2$CMe)(μ-DPPM)(μ-PPh$_2$)] (**4**) and [Ph$_2$PCH$_2$PR$_3$][BPh$_4$] (**5**). The triphenylphosphine products, **4a** and [**5a**]$^+$, can be prepared alternatively from the thermal reaction of either [**2a**]$^+$ or [**3a**]$^+$ with excess PPh$_3$. Reaction of [**1**]$^+$ with a stoichiometric amount of PPh$_3$ helped to reveal the presence of a cationic intermediate [Ru$_2$(CO)$_2$(PR$_3$)(μ_1,η^2-CH$_2$PPh$_2$)(μ-O$_2$CMe)(μ-DPPM)(μ-PPh$_2$)]$^+$ ([**6**]$^+$), produced apparently from [Ru$_2$(CO)$_3$(PR$_3$)(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ ([**3c**]$^+$). An electronic supersaturation rather than a transient unsaturation is proposed to account for the observed P−CH$_2$ bond cleavage taking place for [**3c**]$^+$. Both the spectroscopic and the X-ray structural results of the triphenylphospine intermediate [**6a**][BPh$_4$] indicate the presence of two isomeric forms in an approximate ratio of 1:5, differing probably in the relative orientation of the CH$_2$PPh$_2$ group with respect to the carboxylato bridge.

Introduction

Bis(diphenylphosphino)methane (DPPM), one of the most commonly used diphosphine ligands in "stabilizing" the integrity of di- and polynuclear transition-metal frameworks,[1] is known to undergo a thermally oxidative P−C bond cleavage.[2−4] It is normally reported that carbonyl loss is a key step, creating electron deficiency and then leading to the cleavage. However, this is largely unsubstantiated.

In an extended study of the thermal substitution reactions[5] of a cation [Ru$_2$(CO)$_4$(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ ([**1**]$^+$) with various neutral two-electron nucleophiles, described below, we found some evidence indicating that the cleavage is more sensitive to an electronic supersaturation[6] rather than a transient unsaturation. The cleavage pattern is quite unusual, involving a difficult P−C(sp^3) bond breaking[7] from Ph$_2$PCH$_2$PPh$_2$ into Ph$_2$P- and CH$_2$PPh$_2$-coordinated fragments. Importantly, the latter fragment was found to adopt a side-on coordination mode on only one of the two metal centers in an isolated key intermediate. Further reaction with a phosphine, releases this fragment as a cation [PR$_3$CH$_2$PPh$_2$]$^+$.

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† Deceased April 1, 1996.

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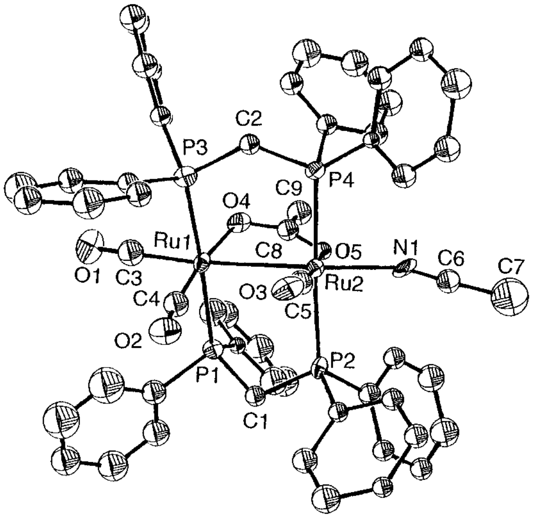

Figure 1. ORTEP plot of [**3a**]$^+$ with 50% thermal ellipsoids. Selected bond lengths: Ru(1)−Ru(2) = 2.830(4), Ru(1)−P(1) = 2.402(10), Ru(1)−P(3) = 2.380(10), Ru(1)−O(4) = 2.150(22), Ru(1)−C(3) = 1.914(42), Ru(1)−C(4) = 1.805(42), Ru(2)−P(2) = 2.367(10), Ru(2)−P(4) = 2.349(10), Ru(2)−O(5) = 1.764(37), Ru(2)−N(1) = 2.125(30), Ru(2)−C(5) = 1.764(37) Å. Selected bond angles: Ru(2)−Ru(1)−P(1) = 89.6(2), Ru(2)−Ru(1)−P(3) = 92.0(3), Ru(2)−Ru(1)−C(3) = 172.7(13), Ru(2)−Ru(1)−C(4) = 93.3(12), Ru(2)−Ru(1)−O(4) = 80.5(6), Ru(1)−Ru(2)−P(2) = 93.0(2), Ru(1)−Ru(2)−P(4) = 90.9(2), Ru(1)−Ru(2)−N(1) = 165.5(7), Ru(1)−Ru(2)−C(5) = 93.4(12), Ru(1)−Ru(2)−O(5) = 81.2(5), N(1)−C(6)−C(7) = 177.9(46), O(4)−Ru(1)−C(4) = 173.1(14), O(5)−Ru(2)−C(5) = 174.5(12)°.

Results and Discussion

The specific thermal lability of two axial carbonyls in bimetallic Ru(I) complexes has been recently observed in many instances.[8] Hence, it is not surprising to observe that thermal reaction of [**1**]$^+$ with MeCN or P(OMe)$_3$ follows a similar route, producing [Ru$_2$(CO)$_2$L$_2$(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ (L = MeCN ([**2a**]$^+$) or P(OMe)$_3$ ([**2b**]$^+$)). However, as reflected in the IR spectra measured sequentially for the reactions in solution, the presumed intermediate, [Ru$_2$(CO)$_3$(MeCN)(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ ([**3a**]$^+$), should have enough thermal stability to be isolated or prepared via an alternative route. Indeed, this intermediate can be obtained almost immediately and quantitatively by treatment of [**1**]$^+$ with 1 equiv of Me$_3$NO in MeCN at ambient temperature. The structure of [**3a**]$^+$ was also confirmed by X-ray diffraction methods to have the MeCN ligand at one axial position (Figure 1). Subsequent reaction of [**3a**]$^+$ with MeCN either at reflux or with addition of another 1 equiv of Me$_3$NO allows formation of [**2a**]$^+$.

The Ru−Ru distance of 2.830(4) Å found in [**3a**]$^+$ is slightly shorter than that of 2.841(1) Å observed in [**1**]$^+$,[9] but the difference between these two values is not significant. The slightly longer Ru−N distance of 2.125(30) Å in [**3a**]$^+$ relative to the typical values between 2.097(6) and 2.107(6)[9,10] and the bended Ru−Ru−N skeleton with ∠Ru(1)−Ru(2)−N(1) = 165.5(7)° reflect the weak coordination between the hard MeCN ligand and the soft Ru(I) metal center in [**3a**]$^+$. As a result, two linkages, O−Ru−CO, formed by two acetate oxygen atoms, two Ru atoms, and two *trans*-equatorial carbonyls, are almost collinear with ∠O(4)−Ru(1)−C(4) = 173.1(14)° and ∠O(5)−Ru(2)−C(5) = 174.5(12)°. With ligation of a softer but bulkier ligand, either a phosphite such as P(OMe)$_3$ or a phosphine (PR$_3$), relative to MeCN, the collinear feature will not be kept, especially for the equatorial carbonyl group closer to the phosphite or phosphine ligand in [Ru$_2$(CO)$_3$(L)(μ-O$_2$CMe)(μ-DPPM)$_2$]$^+$ (L = P(OMe)$_3$ ([**3b**]$^+$) or PR$_3$ ([**3c**]$^+$)); this carbonyl would be forced to bend back from the ligand and from the collinearity more than the other one. In other words, structures [**3b**]$^+$ and [**3c**]$^+$ are believed to be more distorted than structure [**3a**]$^+$. With this distortion, the equatorial carbonyl groups may not dissipate the accumulated electron density in the diruthenium center due to the ligation of the *trans*-acetate group in [**3b**]$^+$ or [**3c**]$^+$ as efficiently as in [**3a**]$^+$.

In contrast to the straightforward reaction of [**1**]$^+$ with MeCN or P(OMe)$_3$, those of [**1**]$^+$ with an excess amount of various phosphines in MeCN appeared complicated, as shown in the ^{31}P{^{1}H} NMR spectra of the reaction solution measured sequentially. However, isolation of a key intermediate and all the final products formed enlightens our understanding about the reactions. The reaction products are unexpected to have two components with and without metals, including neutral compounds in a general formula of [Ru$_2$(CO)$_2$(PR$_3$)$_2$(μ-O$_2$CMe)(μ-DPPM)(μ-PPh$_2$)] (PR$_3$ = PPh$_3$ (**4a**), PPh$_2$Me (**4b**), and PEt$_3$ (**4c**)) and salts [Ph$_2$PCH$_2$PR$_3$][BPh$_4$] (PR$_3$ = PPh$_3$ (**5a**), PPh$_2$Me (**5b**), and PEt$_3$ (**5c**)). Compounds **4a** and [**5a**]$^+$ can be obtained alternatively from the thermal reaction of either [**2a**]$^+$ or [**3a**]$^+$ with excess PPh$_3$, indicating that these two cations are probably involved in the formation of **4** and [**5**]$^+$ from [**1**]$^+$ in MeCN. The structures of **4a**−**c** can be deduced as shown in Scheme 1 on the basis of the observed diamagnetic property, ^{31}P NMR spectral data,[3,4,11,12] and the structure of one of the precursor compounds [Ru$_2$(CO)$_2$(PPh$_3$)(μ_1,η^2-CH$_2$PPh$_2$)(μ-O$_2$CMe)(μ-DPPM)(μ-PPh$_2$)][BPh$_4$] (**6a** or [**6a**][BPh$_4$]), the key intermediate (Figure 2) which can be easily separated from a trace amount of an insoluble by-product, **4a**, in the reaction between [**1**]$^+$ and a stoichiometric amount of PPh$_3$. Conversion from [**6a**]$^+$ to **4a** and [**5a**]$^+$ by reacting with excess PPh$_3$ was found almost quantitatively. Apparently, the increased electron density accumulated in the diruthenium center after the ligation of one phosphine ligand, softer than MeCN or P(OMe)$_3$, in the presumed intermediate, [**3c**]$^+$, accompanied with the worse dissipation of this electron density in [**3c**]$^+$ by the distorted carbonyls as described above, may cause an electronic *supersaturation*,[6] initiating the oxidative Ph$_2$P−CH$_2$-PPh$_2$ bond cleavage to produce Ph$_2$P- and CH$_2$PPh$_2$-coordinated fragments in [**6a**]$^+$. The former fragment was found to act as a bridging ligand for the two Ru atoms, whereas the latter one coordinates with only one Ru atom in a side-on geometry. The O−Ru−CO linkages in [**6a**]$^+$ regain collinearity from those in [**3c**]$^+$, with ∠O(3)−Ru(1)−C(1) = 173.7(5)° and ∠O(4)−Ru(2)−C(2) = 178.8(4)° (Figure 2). The intermediates, [**6a**]$^+$, [**6b**]$^+$,

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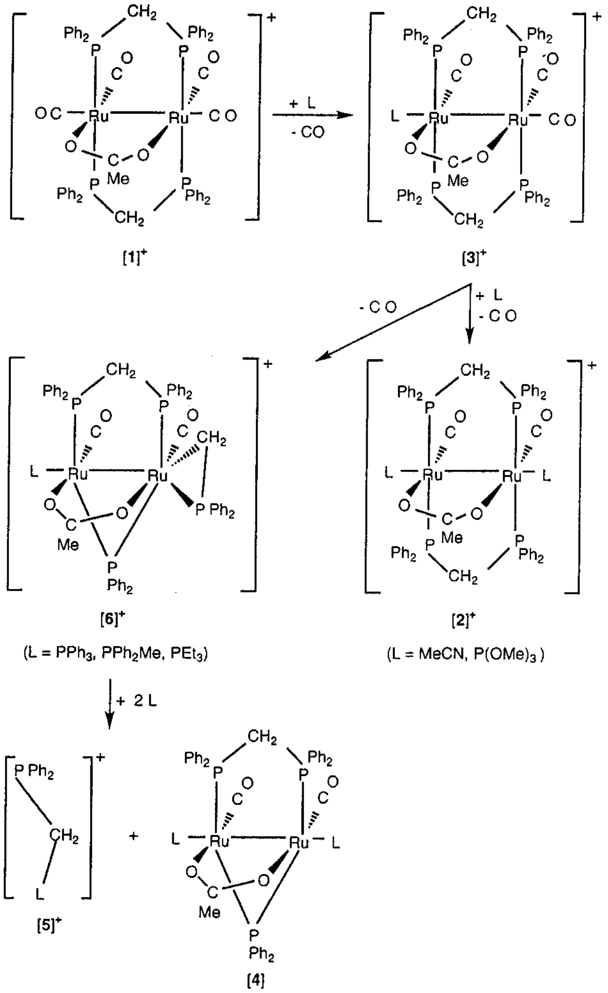
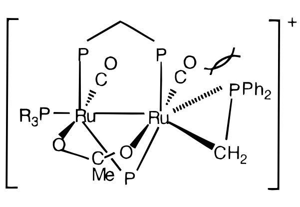
Scheme 1

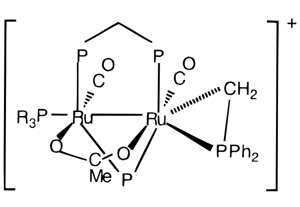


and [**6c**]$^+$, display electrophilic behavior, reacting with excess phosphine (PR_3) to afford **4** and [**5**]$^+$ (Scheme 1).

Although a ^1H NMR spectrum of **6a**, measured in acetone-d_6, indicates apparently one isomeric form, the corresponding IR and $^{31}P\{^1H\}$ NMR solution spectra show the possible presence of two different isomers, **A** and **B**, illustrated by four carbonyl stretching bands in the IR spectrum and two similar sets of phosphorus multiplets with different intensity and slightly different chemical shifts in this NMR spectrum. If an inverse-gated $^{31}P\{^1H\}$ NMR spectrum was recorded (i.e., without NOE), the integration of the multiplets shows a ratio of **A**/**B** close to 1:5. The spectrum (Figure S1) is deposited as Supporting Information. Attempts to separate the two isomers for further characterization unfortunately failed. However, with the structure of one isomer determined by X-ray diffraction methods (Figure 2), it is probable true that the difference between the two isomeric forms is in the relative orientation of the CH_2PPh_2 group with respect to the carboxylato bridge, and the ORTEP shown in this figure is probably the major isomeric form **B** having less repulsive interactions between the CH_2PPh_2 group and the nearby carbonyl. Two similar isomers are believed to be present also for the presumed intermediate, **6b** or **6c**. The nonbonded distances between the μ-PPh_2 phosphorus atom, P(3), and the DPPM phosphorus atoms, P(1) and P(5), are different, with $d(P(3)\cdots P(1)) = 4.296$ Å and $d(P(3)\cdots P(5)) = 4.558$ Å. If we assume that the coupling constant $J_{P(3),P(1)}$ is smaller than $J_{P(3),P(5)}$, an NMR simulation program may help to give $J_{P(1),P(2)} = 43.35$, $J_{P(1),P(3)} = 17.49$, $J_{P(1),P(4)} = 47.52$, $J_{P(1),P(5)} = -113.42$, $J_{P(2),P(3)} = 35.36$, $J_{P(2),P(4)} = 15.70$, $J_{P(2),P(5)} = -101.27$, $J_{P(3),P(4)} = 175.64$, $J_{P(3),P(5)} = 22.00$, and $J_{P(4),P(5)} = 33.03$ Hz and $\delta_{P(1)} = 26.3$, $\delta_{P(2)} = -10.5$, $\delta_{P(3)} = 179.5$, $\delta_{P(4)} = 11.8$, and $\delta_{P(5)} = 51.4$.[13]



A



B

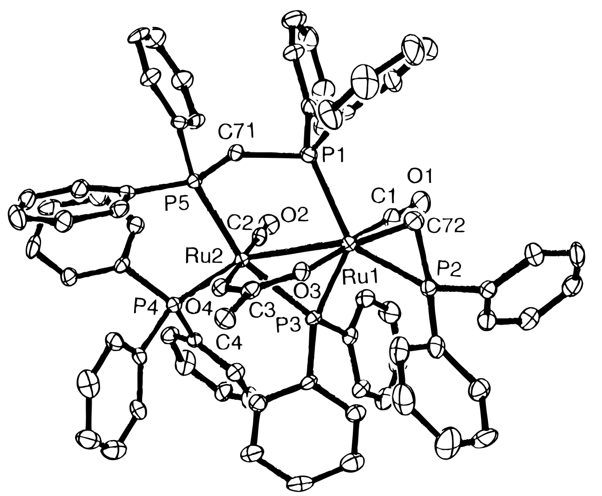


Figure 2. ORTEP plot of [**6a**]$^+$ with 50% thermal ellipsoids. Selected bond lengths: Ru(1)–Ru(2) = 2.999(1), Ru(1)–C(72) = 2.204(13), Ru(1)–P(1) = 2.386(3), Ru(1)–P(2) = 2.329(3), Ru(1)–P(3) = 2.395(3), Ru(2)–P(3) = 2.299(3), Ru(2)–P(4) = 2.361(3), Ru(2)–P(5) = 2.423(2), P(2)–C(72) = 1.742(12), Ru(1)–O(3) = 2.113(7), Ru(2)–O(4) = 2.135(8), Ru(1)–C(1) = 1.833(14), Ru(2)–C(2) = 1.833(13) Å. Selected bond angles: Ru(2)–Ru(1)–P(1) = 79.5(1), Ru(2)–Ru(1)–P(2) = 145.8(1), Ru(2)–Ru(1)–P(3) = 48.9(1), Ru(2)–Ru(1)–C(1) = 105.8(5), Ru(2)–Ru(1)–O(3) = 80.1(2), Ru(1)–Ru(2)–P(3) = 51.7(1), Ru(1)–Ru(2)–P(4) = 158.6(1), Ru(1)–Ru(2)–P(5) = 98.9(1), Ru(1)–Ru(2)–C(2) = 100.2(3), Ru(1)–Ru(2)–O(4) = 79.2(2), P(2)–Ru(1)–C(72) = 45.1(3), Ru(1)–C(72)–P(1) = 71.3(4), Ru(1)–P(2)–C(72) = 63.6(4), O(3)–Ru(1)–C(1) = 173.7(5), O(4)–Ru(2)–C(2) = 178.8(4)°.

The $Ph_2P{-}CH_2$ bond length (i.e., $d(P(2){-}C(72))$) of 1.742(12) in **6a** is much shorter than that of 1.787(6) Å in $[Fe_2(CO)_4(\mu\text{-DPPM})(\mu\text{-PPh}_2)(\mu_2,\eta^2\text{-CH}_2PPh_2)]$[3a] or that of 1.81(1) Å in $[Mo_2(\eta\text{-C}_5H_5)_2(CO)(\mu\text{-I})(\mu\text{-PPh}_2)(\mu_2,\eta^2\text{-CH}_2PPh_2)]$.[4] By comparison with the singly bonded $P{-}CH_3$ distance of 1.843 Å,[14] the three $P{-}CH_2$ distances are indicative of a P–C bond order greater than unity. As shown by various multiplets in NMR spectra, compound **6a** is diamagnetic. It is hence evident that the formal oxidation state for each Ru atom is two. Thus, the ligated "(diphenylphosphino)carbene" group should better be viewed as a four-electron anionic donor (i.e., $PPh_2CH_2^-$) in [**6a**]$^+$, and a conventional electron-count-

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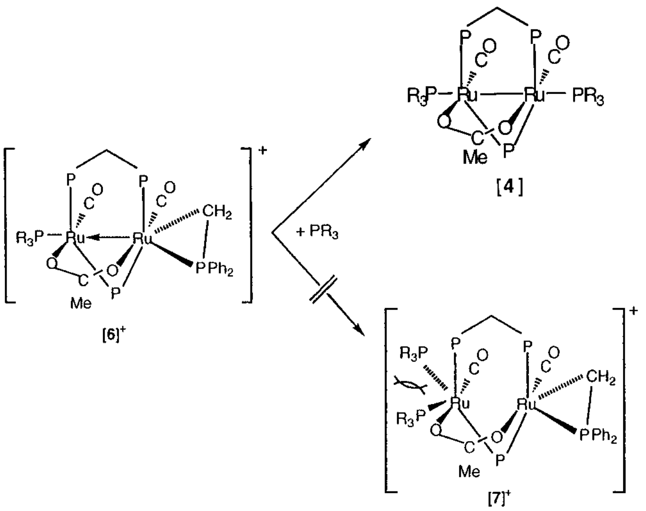
(13) Spectral Simulation gNMR, version 3.6; Cherwell Scientific Publishing Limited: Oxford, U.K., 1995.

(14) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford: New York, 1984; p 846.

Scheme 2



ing system would predict a single Ru−Ru bond for this 34-electron species. This view appears compatible with the more upfield P(1) relative to P(5). The long Ru−Ru bond with d(Ru−Ru) = 2.999(1) Å may be classified as a dative bond, donating an electron pair from the 18-electron Ru(1) center to the 16-electron Ru(2) center.[5,15] However, reactions of [**6**]$^+$ toward PR_3 are not typical for a dinuclear compound with a "dative" metal−metal bond,[12] as demonstrated by that of [**6a**]$^+$ with PPh_3 not to give a Ru(II) adduct such as $[Ru_2(CO)_2(PR_3)_2(\mu\text{-}O_2CMe)(\mu\text{-DPPM})(\mu\text{-}PPh_2)(\mu_1,\eta^2\text{-}CH_2PPh_2)]^+$ ([**7**]$^+$) but to give a reduced Ru(I) product with PPh_2CH_2 eliminated, $[Ru_2(CO)_2(PR_3)_2(\mu\text{-}O_2CMe)(\mu\text{-DPPM})(\mu\text{-}PPh_2)]$ ([**4**]). The elimination of the PPh_2CH_2 group as phosphonium salt $[Ph_2PCH_2PR_3][BPh_4]$ with the reduction of the metal center in [**6**]$^+$ is somewhat surprising, but similar cases were either reported or proposed previously.[16] Lack of formation of an adduct such as [**7**]$^+$ is probably caused by the sterically unfavorable impedance, especially between two bulky phosphine groups (Scheme 2).

Conclusions

The thermal oxidative P−C(sp^3) bond cleavage of a bridging DPPM ligand from a cationic dinuclear complex [**1**]$^+$ can be made to occur by addition of a phosphine, but not a phosphite or MeCN, indicating apparently that the cleavage is more sensitive to an electronic supersaturation[6] rather than a transient unsaturation described previously.[2−4] As revealed in an isolated key intermediate, [**6a**]$^+$ (Figure 2), the Ph_2P−CH_2PPh_2 bond cleavage produces μ-Ph_2P- and μ_1,η^2-(CH_2PPh_2)-coordinated fragments. By reaction with excess phosphine, the latter fragment can be released as a cation [**5a**]$^+$, with concomitant formation of a neutral phosphido complex, [**4a**] (Scheme 1). Thermal reactions of other cationic diruthenium compounds containing different bidentate ligands with two-electron nucleophiles are currently being carried out in our laboratory.

Experimental Section

General Comments. All solvents were dried and purified by standard methods [ethers, paraffins, and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2; alcohols from the corresponding alkoxide] and were freshly distilled under nitrogen immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double manifold providing vacuum and nitrogen. Reagents were used as supplied by Aldrich. ^1H and ^{31}P NMR spectra were measured on a Bruker AMC-400 or a Varian Unity Plus-400 (^1H, 400 MHz; ^{31}P, 162 MHz) or a Bruker AC-200 (^1H, 200 MHz) NMR spectrometer. ^1H chemical shifts (δ in ppm, J in Hz) are defined as positive downfield relative to internal $MeSi_4$ (TMS) or the deuterated solvent, while ^{31}P chemical shifts are defined as positive downfield relative to external 85% H_3PO_4. The IR spectra were recorded on a Hitachi Model 270−30 or Bio-Rad FTS 175 instrument. The following abbreviations were used: vs, very strong; s, strong; m, medium; w, weak; s, singlet; d, doublet; t, triplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; m, multiplet; br, broad unresolved signal. Microanalyses were carried out by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

Synthesis of $[Ru_2(CO)_2(MeCN)_2(\mu\text{-}O_2CMe)(\mu\text{-DPPM})_2][BPh_4]_2$ (2a). Method 1. A stirred solution of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(\mu\text{-DPPM})_2][BF_4]$ (**1**)[9] (0.110 g, 0.090 mmol) in MeCN (15 mL) was heated under reflux for 12 h, and 0.080 g of $NaBPh_4$ (0.234 mmol) was then added to the mixture. The resultant solution was stirred at ambient temperature for 0.5 h to effect the metathesis reaction. The solvent was removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a yellow product (0.124 g, 93%).

Method 2. To a stirred solution of **1** (0.306 g, 0.249 mmol) in MeCN (10 mL) was added dropwise 5 mL solution of $Me_3NO\cdot2H_2O$ (0.062 g, 0.550 mmol) dissolved in MeCN. After 2 h, 0.200 g of $NaBPh_4$ (0.585 mmol) was added to the solution. The solvent was removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a yellow product (0.322 g, 87%). Alternatively, compound **2a** can be prepared by a procedure similar to method 2 but in a shorter period of time (ca. 1.5 h), using equimolar amounts of **3a**, described below, and $Me_3NO\cdot2H_2O$ in MeCN at ambient temperature. The yield is 94%. Anal. Calcd for $C_{82}H_{73}BN_2O_4P_4Ru_2$: C, 66.22; H, 4.95; N, 1.88. Found: C, 65.82; H, 5.15; N, 1.89. ^1H NMR (25 °C, acetone-d_6, 400 MHz): 1.27 (3 H, s), 2.02 (6 H, s), 3.75 (2 H, m), 4.37 (2 H, m), 6.74−7.66 (60 H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): 25.72 (4 P, s). IR (CH_2Cl_2): ν_{CO}, 1927 s; 1885 w cm^{-1}.

Synthesis of $[Ru_2(CO)_2(P(OMe)_3)_2(\mu\text{-}O_2CMe)(\mu\text{-DPPM})_2][BPh_4]_2$ (2b). To a stirred solution of **1** (0.142 g, 0.116 mmol) in MeCN (25 mL) was added excess $P(OMe)_3$ (ca. 0.5 mL). The solution was heated under reflux for 7 h, and 0.212 g of $NaBPh_4$ (0.619 mmol) was then added to the mixture. The resultant solution was stirred at ambient temperature for 0.5 h to effect the metathesis reaction. The solvent was removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a yellow product (0.148 g, 77%). Anal. Calcd for $C_{84}H_{85}O_{10}P_6Ru_2$: C, 61.02; H, 5.18. Found: C, 60.69; H, 5.28. ^1H NMR (25 °C, $CDCl_3$, 200 MHz): 0.97 (3 H, s), 2.79 (18 H, t, J = 5.3), 4.28 (2 H, m), 4.45 (2 H, m), 6.85−7.59 (60

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H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): 21.45 (4 P, t, J = 24.7), 119.88 (2 P, quintet). IR (CH_2Cl_2): ν_{CO}, 1929 s; 1886 w cm^{-1}.

Synthesis of [$Ru_2(CO)_3(MeCN)(\mu$-$O_2CMe)(\mu$-DPPM$)_2$][BPh_4]$_2$ (3a). To a stirred solution of **1** (0.133 g, 0.108 mmol) in MeCN (10 mL) was added dropwise 2 mL solution of $Me_3NO{\cdot}2H_2O$ (0.0121 g, 0.109 mmol) dissolved in MeCN. After 10 min, 0.194 g of $NaBPh_4$ (0.567 mmol) was added to the solution. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a yellow product (0.145 g, 91%). Anal. Calcd for $C_{81}H_{70}BNO_5P_4Ru_2$: C, 65.99; H, 4.79; N, 0.95. Found: C, 65.68; H, 4.81; N, 0.96. ^1H NMR (25 °C, CD_3CN, 400 MHz): 0.80 (3 H, s), 1.95 (3 H, s), 3.88 (1 H, m), 4.13 (1 H, m), 4.34 (1 H, m), 4.58 (1 H, m), 5.41−7.48 (60 H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): 27.96 (2 P, m), 28.53 (2 P, m). IR (CH_2Cl_2): ν_{CO}, 2006 s; 1950 s; 1902 w cm^{-1}.

Reaction of [$Ru_2(CO)_4(\mu$-$O_2CMe)(\mu$-DPPM$)_2$][BF_4] (1) with Excess Phosphine. With PPh_3. A stirred solution of**1** (0.174 g, 0.142 mmol) and PPh_3 (0.311 g, 1.187 mmol) in MeCN (40 mL) was heated under reflux for 61 h. The orange-yellow precipitate formed during the reaction was filtered out, washed with MeCN (5 mL) three times, and dried under vacuum to give 0.168 g (84%) of compound **4a**. A 0.107 g amount of $NaBPh_4$ (0.313 mmol) was added to the filtrate, and the solution was stirred for 0.5 h to effect the metathesis reaction. The solvent was removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a pale yellow product **5a** (0.087 g, 78%).

With PPh_2Me. A stirred solution of **1** (0.144 g, 0.117 mmol) and PPh_2Me (ca. 0.2 mL) in MeCN (15 mL) was heated under reflux for 3 h. The solvent was removed under vacuum. The solid residue was extracted with Et_2O six times. The remaining residue was dissolved in 5 mL of MeOH. Upon addition of 0.100 g of $NaBPh_4$ (0.292 mmol), a pale yellow precipitate formed, which was collected, washed with 5 mL of MeOH and 5 mL of Et_2O, and dried under vacuum to give **5b** (0.058 g, 69%). The ether solvent was then removed from the extract. Recrystallization from CH_2Cl_2/MeOH gave a yellow product **4b** (0.110 g, 73%).

With PEt_3. Compounds **4c** and **5c** were prepared in yields of 63% and 78%, respectively, by a procedure similar to that used for **4b** and **5b**. Anal. Calcd for $C_{77}H_{65}O_4P_5Ru_2$ (**4a**): C, 65.53; H, 4.64. Found: C, 65.64; H, 4.65. ^1H NMR (25 °C, $CDCl_3$, 400 MHz): 0.86 (3 H, s), 3.42 (1 H, m), 3.78 (1 H, br), 6.46−7.53 (60 H, m). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$, 162 MHz): 24.5 (2 P, d, J = 182), 31.4 (2 P, s), 153.7 (1 P, t). IR (CH_2Cl_2): ν_{CO}, 1904 s; 1869 w cm^{-1}. Anal. Calcd for $C_{67}H_{61}O_4P_5Ru_2$ (**4b**): C, 62.52; H, 4.78. Found: C, 62.64; H, 4.90. ^1H NMR (25 °C, $CDCl_3$, 200 MHz): 0.86 (3 H, s), 1.51 (6 H, br), 4.01 (2 H, m), 6.75−7.44 (50 H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): 12.0 (2 P, s), 26.6 (2 P, d, J = 181), 150.7 (1 P, t). IR (CH_2Cl_2): ν_{CO}, 1903 s; 1866 w cm^{-1}. Anal. Calcd for $C_{53}H_{65}O_4P_5Ru_2$ (**4c**): C, 55.68; H, 5.83. Found: C, 55.68; H, 5.98. ^1H NMR (25 °C, acetone-d_6, 400 MHz): 0.77 (18 H, m), 1.39 (3 H, m), 1.60 (12 H, m), 4.06 (2 H, m), 7.07−7.58 (30 H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): 11.8 (2 P, s), 27.7 (2 P, d, J = 182), 148.5 (1 P, t). IR (CH_2Cl_2): ν_{CO}, 1900 s; 1862 w cm^{-1}. Anal. Calcd for $C_{55}H_{47}BP_2$ (**5a**): C, 84.61; H, 6.07. Found: C, 83.93; H, 6.02. ^1H NMR (25 °C, CD_3CN, 400 MHz): 4.00 (2 H, dd, J = 14.4, 0.8), 6.80−7.73 (45 H, m). $^{31}P\{^1H\}$ NMR (25 °C, CD_3CN, 162 MHz): −29.0 (1 P, d, J = 62), 21.9 (1 P, d). Anal. Calcd for $C_{50}H_{45}BP_2$ (**5b**): C, 83.56; H, 6.31. Found: C, 83.33; H, 6.38. ^1H NMR (25 °C, acetone-d_6, 400 MHz): 2.67 (2 H, d, J = 13.6), 4.08 (2 H, d, br, J = 15.2), 6.74−7.90 (40 H, m). $^{31}P\{^1H\}$ NMR (25 °C, CD_3CN, 162 MHz): −29.0 (1 P, d, J = 62), 21.9 (1 P, d). Anal. Calcd for $C_{43}H_{47}BP_2$ (**5c**): C, 81.13; H, 7.44. Found: C, 81.20; H, 7.44. ^1H NMR (25 °C, acetone-d_6, 400 MHz): 1.22 (9 H, dt, J = 18.8, 7.6), 2.33 (6 H, dq, J = 12.8, 7.6), 3.34 (2 H, d, J = 14.8), 6.75−7.54 (30 H, m). $^{31}P\{^1H\}$ NMR (25 °C, CD_3CN, 162 MHz): −30.2 (1 P, d, J = 48), 40.5 (1 P, d).

Table 1. Crystal Data

compd	**3a**$\cdot{}^1/_2C_6H_{14}{\cdot}H_2O$	**6a**$\cdot 2CH_3OH{\cdot}H_2O$
formula	$C_{84}H_{76}BNO_6P_4Ru_2$	$C_{98}H_{92}BO_7P_5Ru_2$
fw	1532.29	1739.4
color, habit	orange irregular	orange-yellow bladed
diffractometer used	Siemens P4	Siemens SMART-CCD
space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	17.605(7)	15.681(2)
b, Å	20.434(4)	16.233(2)
c, Å	21.558(2)	21.548(2)
α, deg	90	89.67(2)
β, deg	97.870(1)	71.09(2)
γ, deg	90	62.27(2)
V, Å^3	7682(4)	4524.1(9)
Z	4	2
D_{calcd}, gcm^{-3}	1.325	1.277
λ(Mo Kα), Å	0.710 73	0.710 73
F(000)	3152	1788
unit cell detn		
no.; 2θ range, deg	25; 15−16	whole data
scan type	$\theta-\omega$	hemisphere
2θ range, deg	3−45	3−52
h,k,l range	18,22,±23	±18,±19,26
μ(Mo Kα), cm^{-1}	5.3	4.75
cryst size, mm	0.2 × 0.2 × 0.3	0.22 × 0.11 × 0.05
temp, K	298	296
no. of measd reflns	10 390	36 133
no. of unique reflns	10 011	15 390
no. of obsd reflns (N_o)	2314 (>5σ)	8705 (>3σ)
R,[a] R_w[a]	0.084, 0.092	0.077, 0.075
GOF[a]	1.26	1.43
refinement program	SHELXTL-PLUS	SHELXTL-PLUS
no. of ref params (N_p)	308	993
weighting scheme	$[\sigma^2(F_o) + 0.0015F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0005F_o^2]^{-1}$
$(\Delta\rho)_{max}$, e Å^{-3}	0.61	1.33
$(\Delta\rho)_{min}$, e Å^{-3}	−0.65	−1.02

[a] $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

Reaction of 1, 2a, or 3a with a Stoichiometric Amount of Phosphine. Since the reactions gave a similar mixture of different products, only one typical reaction for **2a** was described below. A stirred solution of **2a** (0.142 g, 0.096 mmol) and PPh_3 (0.252 g, 0.096 mmol) in MeCN (15 mL) was heated under reflux for 7 h. About 0.0021 g (2%) of the orange-yellow precipitate **4a**, formed during the reaction, was filtered out, washed with MeCN (5 mL) several times until a colorless filtrate was obtained, and dried under vacuum. A 0.198 g amount of $NaBPh_4$ (0.579 mmol) was added to the filtrate, and the resultant solution was stirred for 0.5 h to effect the metathesis reaction. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave an orange-yellow compound **6a**. The compound was washed with cool MeCN (2 mL) to be rid of any **5a** and dried under vacuum to give 0.101 g (63%). Anal. Calcd for $C_{96}H_{82}BO_4P_5Ru_2$: C, 69.15; H, 4.96. Found: C, 69.46; H, 5.18. ^1H NMR (25 °C, acetone-d_6, 400 MHz): 0.87 (2 H, m), 1.27 (3 H, s), 4.65 (1 H, m), 4.78 (1 H, m), 6.74−7.60 (75 H, m). $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6, 162 MHz): multiplets for isomer **B**, 179.5, 51.4, 26.3, 11.8, −10.5; for minor isomer **A**, 167.9, 47.1, 13.6, 9.1, −17.3. IR (MeCN): ν_{CO}, 2001 w; 1968 w; 1945 w; 1925 s cm^{-1}.

Single-Crystal X-ray Diffraction Studies of 3a and 6a. Suitable single crystals were grown from CH_2Cl_2/hexane or MeCN/Et_2O at room temperature to do the single-crystal structure determination. The X-ray diffraction data for **3a** were measured on a Siemens P4 four-circle diffractometer, and those for **6a** were measured in frames with increasing ω (0.30°/frame) and with the scan speed at 10.00 s/frame on a Siemens SMART-CCD instrument, equipped with a normal focus and 3 kW sealed-tube X-ray source. For data collected on the four-circle diffractometer, three standard reflections were monitored every 500 reflections through the collection. The variation for **3a** was less than 6%. Empirical absorption corrections were carried out on the basis of an azimuthal scan. The structures of **3a** and **6a** were solved by direct methods and refined by a full-matrix least-square procedure using SHELX-TL-

PLUS.[17] In order to keep an optimum data-to-parameter ratio, only non-hydrogen and -carbon atoms were refined anisotropically for **3a**. The other essential details of single-crystal data measurement and refinement are given in Table 1. In the asymmetric unit of the crystals used were found one molecule of water and a half-molecule of hexane in **3a** and two molecules of MeOH and one molecule of water in **6a**. The three hydrogen atoms of MeCN in **3a** were not found in a difference map and not included in the final cycle of the refinement.

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Supporting Information Available: The 162-MHz inverse-gated $^{31}P\{^1H\}$ NMR spectrum of **6a** in acetone-d_6 (Figure S1) and tables of non-hydrogen atomic coordinates and equivalent isotropic displacement coefficients, complete bond lengths and angles, anisotropic displacement coefficients, and hydrogen coordinates and *B* values for **3a** and **6a** (14 pages). Ordering information is given on any current masthead page.

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