Ligand Displacement Reaction of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) with Lewis Bases

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Reactions of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) (COD = cyclooctadiene, C_8H_{12}; COT = cyclooctatriene, C_8H_{10}) with a series of Lewis bases are studied. Treatments of **1** with $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, $P(OEt)_2Ph$, $P(O^iPr)_3$, $P(OMe)Ph_2$, or $P(OEt)Ph_2$ lead to the formation of Ru(η^4-1,5-COD)(η^4-1,3,5-COT)L (**2**) followed by preferential liberation of the 1,5-COD ligand to give COT complexes formulated as Ru(6-η^1:1−3-η^3-COT)L_3 (**3**) and Ru(η^4-1,3,5-COT)L_3 (**4**). Reaction of **1** with $P(OPh)_3$ also gives **2,** but further treatment of this system leads to the liberation of both 1,5-COD and 1,3,5-COT to give a mixture of Ru(η^4-1,5-COD)L_3 (**5**) and Ru(6-η^1:1−3-η^3-COT)L_3 (**3**) and finally gives Ru{$P(OC_6H_4)(OPh)_2$}$_2$-{$P(OPh)_3$}$_2$ (**6h**). In the reaction of **1** with *tert*-butylisonitrile, 1,3,5-COT is initially liberated with concomitant formation of Ru(η^4-1,5-COD)(CN^tBu)$_3$ (**5j**), which further reacts with the liberated 1,3,5-COT, giving eventually Ru(6-η^1:1−3-η^3-COT)(CN^tBu)$_3$ (**3j**). The molecular structure of **5j** determined by X-ray structure analysis reveals that one of the isonitrile ligands has a considerable carbene character. In the presence of excess isonitrile, the homoleptic complex Ru(CN^tBu)$_5$ (**7**) is formed. On the other hand, **1** does not react with poor π-accepting ligands such as NEt_3, pyridine, and (dimethylamino)pyridine as well as bulky phosphorus ligands such as triphenylphosphine and tricyclohexylphosphine. These results suggest that the initial coordination of electron-donating ligands to Ru essentially encourages the dissociation of the 1,5-COD ligand, but the π-accepting ability of the ligand induces the dissociation of the 1,3,5-COT ligand.

Introduction

Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**)[1,2] is regarded as a versatile zerovalent ruthenium complex with two labile cyclic polyene ligands.[3] Complex **1** is known to catalyze remarkable reactions such as [2+2] cross addition of norbornadiene and acetylenes,[4] co-dimerization of acetylenes with 1,3-dienes[5] or alkenes,[6] *Z*-selective formation of butatriene,[7] co-cycloaddition of allylic amine,[8] allylic alkylations,[9] reductive cleavage of allylic esters,[10] tail-to-tail dimerization of acrylonitrile,[11] *Z*-selective isomerization of 2-allylphenol,[12] carbonylation of allylic carbonates,[13] preparation of cyclohexanones from allylic compounds with β-keto esters,[14] and dimerization of norbornadiene involving C−C bond cleavage[15] in the presence of suitable σ-donors or π-acceptors. In these reactions, initial displacement or partial dissociation of the cyclic polyene ligands is considered to be a possible prerequisite entry step. However, the ligand displacement process of **1** by Lewis bases is relatively unexplored to date at a molecular level, although initial facile reaction is usually formation of an adduct Ru(η^4-1,5-COD)(η^4-1,3,5-COT)L, which is followed by various further reactions. Published examples of the ligand

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(1) Abbreviations: COD = cyclooctadiene (C_8H_{12}), COT = cyclooctatriene (C_8H_{10}), DPPM = 1,1-bis(diphenylphosphino)methane ($C_{25}H_{22}P_2$), DMAP = 4-*N*,*N*-dimethylaminopyridiene ($C_7H_{10}N_2$).

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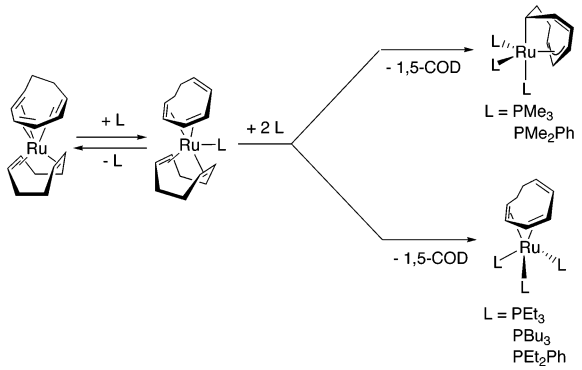
Scheme 1



displacement include reactions of **1** with arene under H_2 giving Ru(η^4-1,5-COD)(η^6-arene),[16−19] with CO giving Ru(η^4-1,5-COD)$(CO)_3$,[20] and with DPPM giving Ru(η^4-1,5-COD)(DPPM-κ^2P,P')(DPPM-κ^1P),[21] where all examples preferentially liberate the 1,3,5-COT ligand without exception. From these results, the 1,3,5-COT ligand had been considered to be more labile than the 1,5-COD ligand in general. Despite these facts, we recently exploited the first examples of exclusive substitution of the 1,5-COD ligand by the reaction of **1** with a series of monodentate tertiary phosphines (Scheme 1).[22,23]

Mitsudo et al. also documented the second example of the preferential liberation of the 1,5-COD ligand by the reaction of **1** with electron-deficient olefins.[15,24] Thus, the 1,5-COD ligand does not always act as a spectator ligand in substitution reaction of **1**, although the process is likely to correlate with the mechanisms of the catalyses promoted by the combination of **1** with Lewis bases. We report herein the reactions of **1** with various monodentate Lewis bases to elucidate the controlling factors in the ligand displacement reaction of **1**.

Results

1. Reaction of 1 with Phosphites, Phosphonites, and Phosphinites. Ligand substitution reactions of **1** with a series of phosphorus compounds such as alkyl phosphites, phosphonites, and phosphinites were carried out (Scheme 2 and Table 1). When $P(OMe)_3$ was added into a C_6D_6 solution of **1** at 50 °C, complex **1** completely disappeared within 10 min, giving a known monophosphite complex, Ru(η^4-1,5-COD)(η^4-1,3,5-COT){$P(OMe)_3$}

Table 1. Summary for the Reaction of 1 with Trialkyl Phosphite, Phosphonite, and Phosphinites[a]

			yield (%)	
ligand	cone angle (deg)	conv (%)	**3**	**4**
$P(OMe)_3$	107	100	44	49
$P(OEt)_3$	109	100	36	40
$P(OMe)_2Ph$	115	100	13	61
$P(OEt)_2Ph$	116	100	11	77
$P(O^iPr)_3$	130	100	8	48
$P(OMe)Ph_2$	132	100	17	53
$P(OEt)Ph_2$	133	100	16	52

[a] Conditions: **1** (0.049−0.0720 mmol), phosphorus compound (3 equiv), C_6D_6 (0.6 mL), 50 °C, 20−24 h.

(**2a**)[25] (96% yield). Further inspection of the spectrum revealed the formation of an additional small amount of a 6-η^1:1−3-η^3-COT complex, Ru(6-η^1:1−3-η^3-COT)-{$P(OMe)_3$}$_3$ (**3a**) (4% yield). Longer treatment of this system at 50 °C for 24 h eventually gave a mixture of **3a** and Ru(η^4-1,3,5-COT){$P(OMe)_3$}$_3$ (**4a**) in 44% and 49% yields, respectively, by preferential liberation of the 1,5-COD ligand. As shown in Scheme 1, we previously reported the exclusive liberation of the 1,5-COD ligand in the reaction of **1** with monodentate tertiary phosphine, giving either 6-η^1:1−3-η^3-COT or η^4-1,3,5-COT complex depending on the phosphine employed.[22,23] The ^{1}H NMR spectral characteristic of these coordination modes is that the 6-η^1:1−3-η^3-COT ligand has a sequence of 1-, 2-, and 3-C*H* protons in the allylic region (typically δ 3.0−5.0) and the η^4-1,3,5-COT has a couple of low-field resonances (typically δ 4.5−5.0) due to 2- and 3-C*H* and a couple of high-field resonances (typically δ 2.5−3.0) due to 1- and 4-C*H*, which is a reflection of the contribution of the LX_2 ($\pi\sigma_2$) coordination mode (vide infra). Since, in both cases, they have conspicuous uncoordinated olefinic protons (2H) around δ 5.0−6.0, the other resonances can be easily assigned one after another by their spin correlations based on these olefinic protons by use of ^{1}H−^{1}H COSY. Thus, these coordination modes can be unambiguously characterized spectroscopically. For complex **3a**, the uncoordinated olefinic protons assignable to 4- and 5-C*H* appear at δ 5.7−5.8 (m, 2H) and the correlated allylic signals at δ 5.0 (br, 1H) and 4.7 (m, 2H), which are assignable to the 1-C*H* resonance and 2- and 3-C*H* resonances, respectively, indicating the 6-η^1:1−3-η^3-COT coordination mode. On the other hand, complex **4a** shows correlated signals at δ 6.34 (t, 1H) and 5.1−5.3 (m, 3H) assignable to the 5-C*H* and merged 2-, 3-, and 6-C*H*. Although the 1- and 4-C*H* resonances were accidentally obscured by the PO*Me* signals in the ^{1}H NMR spectrum, the ^{1}H−^{1}H COSY clearly indicated these resonances appeared at δ 3.3−3.4. The complex **4a** was therefore characterized as a η^4-1,3,5-COT complex. The corresponding COD complex Ru(η^4-1,5-COD)L_3 was not observed through the reaction. By the preparative-scale reaction of **1** with $P(OMe)_3$, complex **3a** was fortunately isolated as analytically pure white crystals in 18% yield.

The other phosphorus compounds such as $P(OEt)_3$, $P(OMe)_2Ph$, $P(OEt)_2Ph$, $P(O^iPr)_3$, $P(OMe)Ph_2$, and $P(OEt)Ph_2$ also tend to encourage the exclusive liberation

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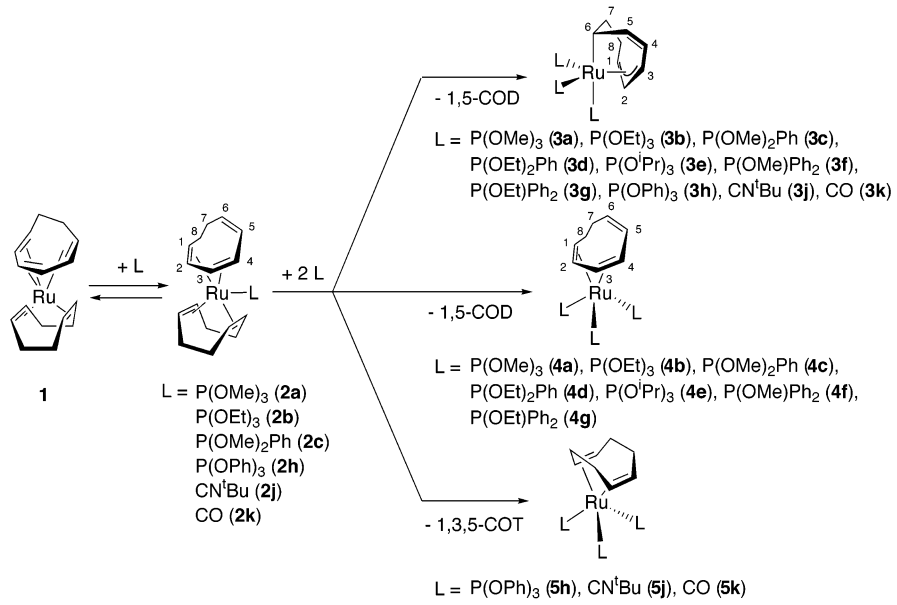
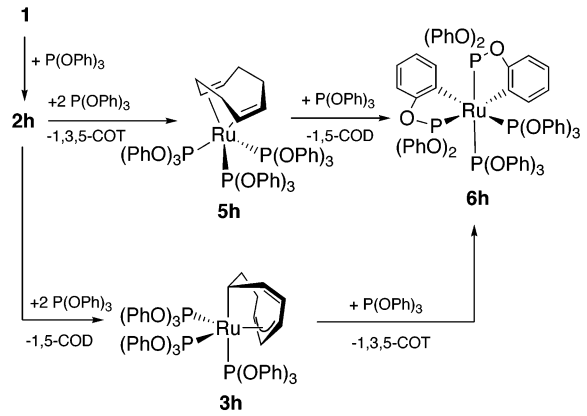
Scheme 2



Scheme 3



of 1,5-COD to form a mixture of **3b**−**g** and **4b**−**g** as shown in Table 1, although these reactions were somewhat complex because of concomitant formation of unidentified species.

When a triaryl phosphite $P(OPh)_3$, which is the strongest π-acceptors among phosphites employed, was reacted with **1**, the substitution reaction proceeded to give Ru(η^4-1,5-COD)(η^4-1,3,5-COT){$P(OPh)_3$} (**2h**), followed by formation of Ru(6-η^1:1−3-η^3-COT){$P(OPh)_3$}$_3$ (**3h**) and Ru(η^4-1,5-COD){$P(OPh)_3$}$_3$ (**5h**), and finally the known orthometalated complex $\overline{Ru\{P(OC_6H_4)(OPh)_2\}_2}$-{$P(OPh)_3$}$_2$ (**6h**)[26] (Scheme 3). When 4 equiv of $P(OPh)_3$ per **1** was reacted at 50 °C for 18 h, a mixture of **3h** and **5h** was formed in 46% and 23% yields, respectively, although they could not be separated from each other.

The NMR study revealed that this reaction initially gave **2h** in quantitative yield, from which both 1,5-COD and 1,3,5-COT were liberated at almost the same rate as one another giving **3h** and **5h** independently. When the 2:1 mixture of **3h** and **5h** was treated with an excess amount of I_2 for 3 h at room temperature, both 1,5-COD (71% based on **5h**) and 1,3,5-COT (82% based on **3h**) were liberated. Further treatment of the mixture of **3h** and **5h** with 3 equiv of $P(OPh)_3$ at 50 °C for 7 days led to the formation of **6h** in 92% yield. Thus, **3h** and **5h** are regarded as intermediates in the formation of **6h**. Two hydrogens lost in this reaction are consumed as both hydrogen gas and hydrogenation of cyclic olefins, since H_2 gas (40%) was detected by Toepler pump and the GLC analysis revealed formation of cyclooctane (30%), 1,3-COD (29%), 1.5-COD (59%), and 1,3,5-COT (41%). The orthometalation probably takes place after formation of a coordinative unsaturated homoleptic phosphite complex such as "Ru{$P(OPh)_3$}$_4$". Similarly, reaction of **1** with 4 equiv of $P(OC_6H_4Cl\text{-}4)_3$ also gave the homoleptic orthometalated complex $\overline{Ru\{P(OC_6H_3\text{-}Cl\text{-}4)(OC_6H_4Cl\text{-}4)_2\}_2}${$P(OC_6H_4Cl\text{-}4)_3$}$_2$ (**6i**) in 41% yield.

2. Reaction of 1 with Isonitrile and CO. Similarly to the above reactions, treatment of **1** with CN^tBu (3 equiv) initially gave Ru(η^4-1,5-COD)(η^4-1,3,5-COT)(CN^t-Bu) (**2j**) in quantitative yield (26% isolated yield). In this case, however, further reaction caused preferential liberation of 1,3,5-COT to give Ru(η^4-1,5-COD)(CN^tBu)$_3$ (**5j**) in 58% yield (Scheme 4).[27] Since pure yellow single crystals of **5j** were obtained from the acetone solution, the molecular structure of **5j** was determined by X-ray structure analysis, and the ORTEP drawing and selected bond distances and angles are shown in Figure 1 and Table 2, respectively.

The molecular structure of **5j** unambiguously indicates that the 1,5-COD ligand remains as a spectator ligand and three isonitrile ligands coordinate to the ruthenium center. It is notable that one of the three isonitrile ligands is significantly bent at N(1) [C(9)−N(1)−C(10) = 132.5(6)°], indicating strong back-donation to this isonitrile ligand from the ruthenium. Consistently, the bond distance Ru(1)−C(9) [1.906(6) Å] is shorter than the other Ru(1)−C(14) [1.941(6) Å] or Ru(1)−C(19) [2.020(6) Å], and N(1)−C(9) [1.210(8) Å]

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(27) Complex **5j** was spectroscopically reported by the treatment of Ru(η^6-naphthalene)(η^4-1,5-COD) with CN^tBu: Bennett, M. A.; Lu, Z.; Wang, X.; Bown, M.; Hockless, D. C. R. *J. Am. Chem. Soc.* **1998**, *120*, 10409.

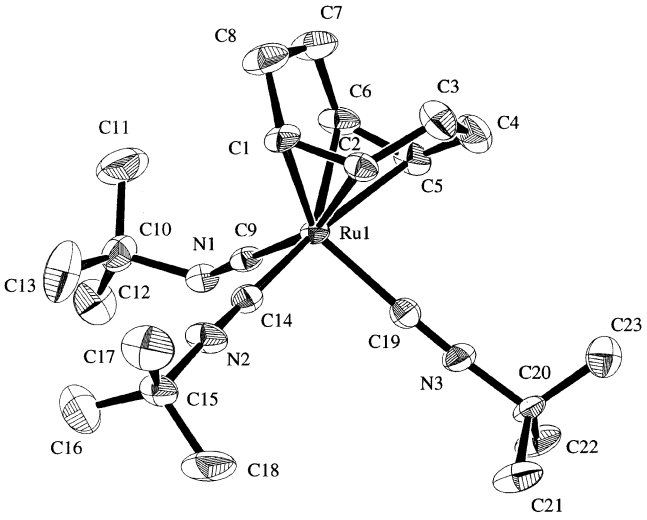


Figure 1. Molecular structure of Ru(η⁴-1,5-COD)(CN^{t}Bu)$_3$ (**5j**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Scheme 4

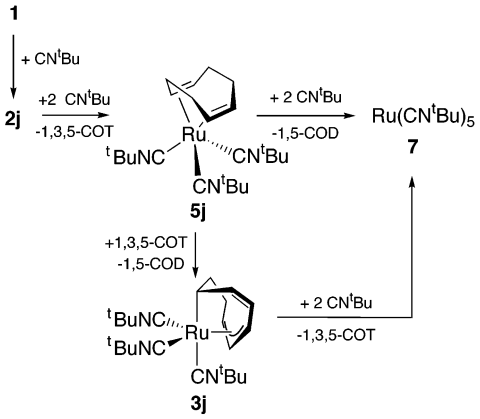


Table 2. Selected Bond Distances and Angles for Ru(η⁴-1,5-COD)(CN^{t}Bu)$_3$ (5j)

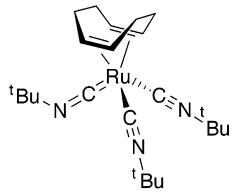
Bond Distances (Å)			
Ru(1)−C(1)	2.179(5)	Ru(1)−C(2)	2.200(6)
Ru(1)−C(5)	2.256(6)	Ru(1)−C(6)	2.265(6)
Ru(1)−C(9)	1.906(6)	Ru(1)−C(14)	1.941(6)
Ru(1)−C(19)	2.020(6)	N(1)−C(9)	1.210(8)
N(1)−C(10)	1.484(8)	N(2)−C(14)	1.163(8)
N(2)−C(15)	1.454(8)	N(3)−C(19)	1.157(8)
N(3)−C(20)	1.446(7)	C(1)−C(8)	1.516(9)
C(2)−C(3)	1.530(9)	C(3)−C(4)	1.52(1)
C(4)−C(5)	1.52(1)	C(5)−C(6)	1.385(10)
C(6)−C(7)	1.496(9)	C(7)−C(8)	1.51(1)

Bond Angles (deg)			
C(9)−N(1)−C(10)	132.5(6)	C(14)−N(2)−C(15)	176.9(7)
C(19)−N(3)−C(20)	176.5(6)	Ru(1)−C(9)−N(1)	178.6(5)
Ru(1)−C(14)−N(2)	178.0(5)	Ru(1)−C(19)−N(3)	176.9(5)

is a little bit longer than the others. The IR spectrum of **5j** shows three ν(CN) bands at 2126, 2102, and 1847 cm^{-1}, the latter low value also reflecting strong π-back-donation. By taking account of these features, one of the isonitrile ligands is considered to have dominant contributions from a carbene structure as depicted in Chart 1.

Similar carbenoic features of the isonitrile ligand are also observed for other reported ruthenium(0) isonitrile complexes.[28] In solution, however, complex **5j** shows one singlet resonance assignable to the ^{t}Bu moiety and three

Chart 1



signals assignable to the *endo*- and *exo*-methylene and a methine protons for 1,5-COD in the ^{1}H NMR. In the ^{13}C{^{1}H} NMR spectrum, one set of signals due to the *C*N*C*Me$_3$ moiety and one set of methylene and methine carbons for 1,5-COD are observed in benzene-d_6. This symmetric feature suggests that three isonitrile moieties are apparently equivalent in solution, due to facile exchange among the three isonitrile ligands and rotation of the 1,5-COD moiety on the NMR time scale.

As shown above, reaction of **1** with 3 equiv of CN^{t}Bu gave the 1,5-COD complex **5j** by preferential liberation of 1,3,5-COT, but unexpectedly further heating of this reaction mixture at 50 °C afforded Ru(6-η¹:1−3-η³-COT)(CN^{t}Bu)$_3$ (**3j**) in 56% yield for 23 h, during which **5j** completely disappeared. Complex **3j** can also be prepared by the reaction of isolated **5j** with 2 equiv of 1,3,5-COT in 54% yield. Therefore, the reaction is considered to be a stepwise reaction. The ligand displacement reaction of 1,5-COD by 1,3,5-COT was retarded not by the added 1,5-COD but by the addition of CN^{t}Bu. This result suggests that an initial loss of CN^{t}Bu to create a vacant site at ruthenium for incoming 1,3,5-COT is an important prior step for the reaction. These experiments show that the initial coordination of isonitrile encourages preferential liberation of 1,3,5-COT in **2j** to give **5j**, but further displacement of the 1,5-COD ligand of **5j** by 1,3,5-COT leading to **3j** may be caused by the higher thermodynamic stability of **3j** than **5j**. When an excess amount of CN^{t}Bu was treated with **1** at 50 °C, a known homoleptic isonitrile complex, Ru(CN^{t}Bu)$_5$ (**7**),[29] was formed in 32% yield. Therefore, the reaction is considered to be a successive reaction in which the once liberated 1,3,5-COT re-coordinated to ruthenium to give **3j** eventually.

Sandrini et al. reported reaction of **1** with CO to form Ru(η⁴-1,5-COD)(CO)$_3$ (**5k**) via Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)(CO) (**2k**), and further treatment of this system with excess CO eventually gave Ru$_3$(CO)$_{12}$ (**8**).[20] When we monitored this experiment by ^{1}H NMR, formation of Ru(6-η¹:1−3-η³-COT)(CO)$_3$ (**3k**) and Ru(η⁴-1,5-COD)(CO)$_3$ (**5k**) was observed after formation of **2k**, although this reaction was not clean due to uncharacterized side reactions. In this reaction, however, formation of both **3k** and **5k** as well as liberation of both 1,5-COD and 1,3,5-COT took place at almost the same rate, suggesting the reaction is not a successive reaction but a parallel one (Scheme 5).

Lewis and co-workers also reported the formation of **5k** by the reaction of Ru$_3$(CO)$_{12}$ with 1,5-COD.[30] Since

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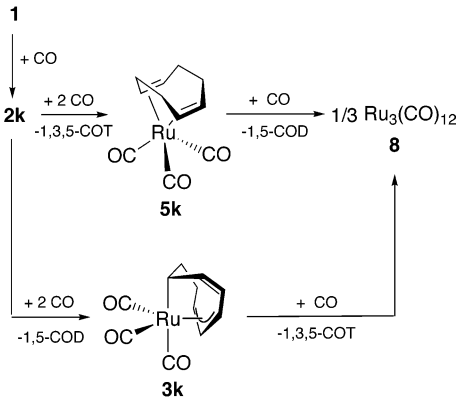
(29) Barker, G. K.; Galas, A. M. R.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 256.

(30) Domingos, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2288.

Scheme 5



they reported that the bicyclic polyene complex Ru(η^4-bicyclo[4.2.0]octa-2,4-diene)$(CO)_3$ is exclusively formed by the reaction of **5k** with 1,3,5-COT and we did not see this product at all in our case, **3k** is formed directly from **2k** but not from **5k**. Although the reaction with CO is a bit complicated, CO is considered to encourage liberation of both 1,5-COD and 1,3,5-COT ligands in **2k**.

3. Reactions of 1 with an N-Donor Ligand. Contrary to the reaction with ligands described above, **1** did not react with nitrogen donors such as NEt_3, pyridine, nor DMAP at all. Complex **1** also did not react with acetonitrile. However, the treatment of **1** with acrylonitrile gave an insoluble complex formulated as Ru(COT)$(AN)_3$ by liberation of 1,5-COD as reported previously as an active species of catalytic dimerization of acrylonitrile by us.[11] Athough insolubility of Ru(COT)-$(AN)_3$ to organic solvent prevented further characterization, acrylonitrile probably coordinates to the ruthenium in an η^2-C═C fashion since acetonitrile did not react with **1** at all.

Discussion

As relatively well established, the reaction of **1** with Lewis bases commonly gives an intermediate formulated as Ru(η^4-1,5-COD)(η^4-1,3,5-COT)L (**2**) as an initial step. Then, displacement of the cyclic polyene ligands is considered to take place. Selectivity was highly dependent on L employed. To rationalize the ligand displacement selectivity, the trends in initial adduct formation and in structural preference in the COT moiety in resulting Ru(COT)L_3 are visualized in Figure 2.[31]

As we have shown for the reactions of tertiary phosphines, only Lewis bases of cone angle smaller than 145° can react with **1** to give monoligand adduct complexes **2**. The sterically bulky ligands such as PPh_3 and PCy_3 did not react at all with **1** probably because of the lack of enough space for coordination on Ru regardless of the electronic properties of the ligands.[22] On the other hand, N-donor ligands also showed no reactivity with **1**. It is worthwhile to note that the following order of π-acceptor strength is generally accepted: CO > RNC > $P(OR)_3$ > PR_3 > RCN > NR_3.[32] Thus, this may be due to lack of π-accepting property

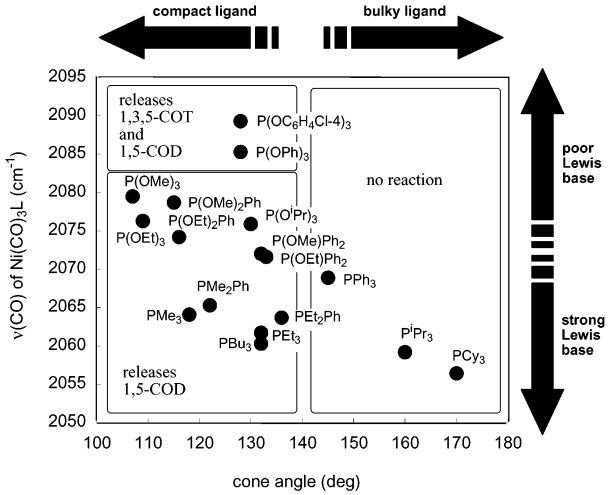
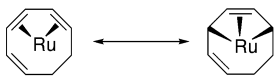


Figure 2. Relationship between ν(CO) value of $Ni(CO)_3L$ (electronic factor) and cone angle (steric factor)[31] in the ligand substitution reactions of **1**.

of these ligands, which discourages coordination to the highly reduced ruthenium center.

It is also interesting to rationalize the trend with which the cyclic polyene ligand is displaced. As seen in Figure 2, a strong donor favors the loss of the COD ligand, giving Ru(COT)L_3 type complexes, but coordination of strong π-acceptor ligands such as triaryl phosphite, isonitrile, and CO causes liberation of the COT ligand. One extreme is highly π-accepting isonitrile, which initially liberates only 1,3,5-COT, giving Ru-(COD)L_3, which slowly displaces again the 1,5-COD ligand by 1,3,5-COT (vide infra). The selectivity is conveniently interpreted by considering the stability of cyclic polyene ligands in the monophosphine adduct **2** in the following way. The more electron-donating ligand such as tertiary phosphines reduces the ruthenium center to cause efficient back-bonding to cyclic polyene ligands. Thus, the LX_2 (or $\pi\sigma_2$) contribution in the COT ligand as shown in eq 1 increases to stabilize the bonding between COT and Ru.



This influence is considered to be larger in COT than that in COD, since back-bonding may be more efficient for the conjugated π-system than the nonconjugated one. On the other hand, if L is highly electron-withdrawing such as isonitrile, electron density at Ru considerably decreases. Therefore, the LX_2 (or $\pi\sigma_2$) contribution in the COT ligand diminishes. It is not clear why displacement of the COT ligand is enhanced in this case, but sterically better matching of the η^4-1,5-COD coordination than the η^4-1,3,5-COT to Ru(0) may be a possible reason because the chelation of nonconjugated dienes is generally believed to introduce rigidity to increase the binding constant to the metal.[33]

The difference in coordination mode of the COT ligand in products is another interesting subject to discuss. Trialkyl phosphites, phosphonites, and phosphinites

(31) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(32) Elschenbroich, C.; Salzer, A. In *Organometallics. A Concise Introduction*, 2nd, revised ed.; VCH: Weinheim, 1992; p 230.
(33) Crabtree, R. H. In *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, 2001; p 129.

essentially liberate 1,5-COD from **2** to give a mixture of Ru(6-η^1:1−3-η^3-COT)L_3 (**3**) and Ru(η^4-1,3,5-COT)L_3 (**4**), whereas monodentate phosphines exclusively gave either **3** or **4** depending on L. The more compact phosphines such as trimethylphosphine and dimethylphenylphosphine gave only **3**, but relatively bulky phosphines such as triethylphosphine afford **4**.[22] Although the product ratios in the cases of trialkyl phosphite, phosphonite, and phosphinite ligands were not accurately estimated, the yield of **3** tends to decrease with decrease in the cone angle of L, as shown in Table 2. Formation of these COT complexes **3** and **4** probably proceeded by a parallel reaction, although the detailed mechanism is not clear at present. One of the evidences for the parallel reaction is that while treatment of **1** with $P(OMe)_3$ gave an approximate 1:1 mixture of **3a** and **4a**, a preliminary reaction of Ru(η^5-cyclooctadieneyl)$_2$ with $P(OMe)_3$ mainly gave **3a**.

Displacement of 1,5-COD ligand in Ru(η^4-1,5-COD)-(CN^tBu)$_3$ (**5j**) by 1,3,5-COT needs some comments. Although 1,3,5-COT is initially displaced by CN^tBu, coordination of three CN^tBu enhances exchange of 1,5-COD by 1,3,5-COT. It is noteworthy that the 1,3,5-COT ligand came back to the Ru as a η^1:η^3-ligand. This is probably due to thermodynamic stability of the product, and this phenomenon can be explained as follows. As shown in the X-ray and IR data of **5j**, one of the isontirile ligands has significant carbene character. Although the reason why only one of the isonitriles has intensively received π-back-donation from ruthenium, this feature may reflect the tendency to become a ruthenium(II) moiety bearing a carbene ligand. Consistently, a part of the driving force for the exchange reaction of η^4-1,5-COD by η^1:η^3-COT may be more effective oxidation of the ruthenium species by forcing the COT ligand to a η^1:η^3-mode. When **5j** was reacted with an excess amount of isontirile, **5j** favors the exchange reaction of 1,5-COD by electron-withdrawing isonitriles to give the homoleptic complex **7**.

In relation to this consideration, it is notable that the Ru(6-η^1:1−3-η^3-COT)P_3 is generally more stable than Ru(η^4-1,5-COD)P_3.[34]

When excess CO, isonitrile, and triaryl phosphites were used, homoleptic complexes were essentially formed as final products by releasing both COD and COT ligands. This complete displacement of the ligand may arise from their extremely strong π-accepting properties, neutralizing the highly reduced zerovalent ruthenium center. In the case of $P(OAr)_3$ further oxidation takes place to give an orthometalation product.

In summary, the displacement reaction of cyclic polyene ligands in **1** with Lewis bases is delicately controlled by π-acidity and steric bulk of the Lewis base. Initial addition of L takes place only when L is compact and π-acidic. When coordinated L is a strong π-acceptor, 1,3,5-COT tends to be displaced by 3L, whereas a weak π-acceptor favors the dissociation of 1,5-COD. Two coordination modes of the 1,3,5-COT ligand in Ru(1,3,5-COT)L_3 are found: one being 6-η^1:1−3-η^3-COT, the other being η^4-1,3,5-COT. The former coordination mode is favored by an electron-donating compact ligand, but the latter by a relatively bulkier ligand. By taking account of these facts, the prime driving force of these ligand displacement reactions seems to be removal of the electron density from the electron-rich ruthenium(0) center.

(34) Komiya, S.; Hirano, M. *Dalton Trans.* **2003**, 1439.

Experimental Section

All manipulations and reactions were performed under dry nitrogen atmosphere with use of standard Schlenk and vacuum line techniques. Benzene, hexane, and pentane were distilled over benzophenone ketyl, and acetone was distilled from Drierite; these solvents were stored under nitrogen. The complex Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**)[2d] was prepared according to literature procedures, but magnetic stirring was used instead of sonication. $P(OC_6H_4Cl\text{-}4)_3$ was prepared by the reaction of PCl_3 with 4-chlorophenol, and 1,3,5-COT was prepared according to literature procedures.[35] All other reagents were obtained from commercial suppliers (Wako Pure Chemical, Kanto, Aldrich, and TCI) and used as received. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL LA 300 (300.4 MHz for ^1H, 121.6 MHz for ^{31}P, and 75.5 MHz for ^{13}C) spectrometer. Benzene-d_6 and toluene-d_8 were distilled over sodium wires and stored under vacuum and were transferred into the NMR tube by bulb-to-bulb distillation. Chemical shifts (δ) are given in ppm, relative to internal TMS for ^1H and ^{13}C and external 85% H_3PO_4 in deuterated water for ^{31}P. All coupling constants are given in Hz. Product yields for reactions in an NMR tube were calculated on the basis of internal $CHPh_3$ or an external C_6D_6 solution of PPh_3 in a flame-sealed capillary. HRMS were performed on a JEOL GC-Mate II by FAB method. Elemental analyses were carried out on a Perkin-Elmer 2400 series II CHN analyzer.

Reactions with P(OMe)$_3$. (a) Complex **1** (125.3 mg, 0.3972 mmol) was placed in a Schlenk tube under nitrogen into which hexane (5 mL) was introduced. Then, $P(OMe)_3$ (141 μL, 1.19 mmol) was added into the solution and warmed at 50 °C for 38 h. After removal of all volatile matters, the resulting white solid was recrystallized from cold pentane (1 mL) to give white crystals of Ru(6-η^1:1−3-η^3-COT){$P(OMe)_3$}$_3$ (**3a**) in 18% yield (40.6 mg, 0.0701 mmol). ^1H NMR (300.4 MHz, C_6D_6): δ 2.0 (br, 1H, 8-CH_2), 2.1 (m, 1H, 8-CH_2), 2.6 (br, 1H, 6-C*H*), 2.8 (br, 1H, 7-CH_2), 2.9 (br, 1H, 7-CH_2), 3.3 (d, J = 11 Hz, 18H, *equatorial*-PO*Me*), 3.6 (dd, J = 9, 1 Hz, 9H, *axial*-PO*Me*), 4.7 (m, 2H, 1- and 3-C*H*), 5.0 (br, 1H, 2-C*H*), 5.7−5.8 (m, 2H, 5- and 6-C*H*). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): δ 145.6 (t, J = 45 Hz, 1P, *axial-P*), 159.6 (dd, J = 61, 45 Hz, 1P, *equatorial-P*), 159.7 (dd, J = 61, 45 Hz, 1P, *equatorial-P*). Anal. Calcd for $C_{17}H_{37}O_9P_3Ru$: C, 35.24; H, 6.44. Found: C, 35.40; H, 6.49.

(b) Complex **1** (15.8 mg, 0.0501 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) was introduced by bulb-to-bulb distillation. $P(OMe)_3$ (17.6 μL, 0.150 mmol) was then added into the NMR tube by a hypodermic syringe, and the NMR tube was warmed to 50 °C. Within 10 min, complex **1** completely disappeared to form Ru(η^4-1,5-COD)(η^4-1,3,5-COT)-{$P(OMe)_3$} (**2a**) and **3a** in 96% and 4% yields, respectively. Further treatment of this system at 50 °C for 24 h gave a mixture of **3a** and Ru(η^4-1,3,5-COT){$P(OMe)_3$}$_3$ (**4a**) in 44% and 49% yields, respectively. Complexes **2a** and **4a** were characterized spectroscopically by use of $^1H-^1H$ COSY and analogy of the related complexes. **2a**: ^1H NMR (300.4 MHz, C_6D_6): δ 1.45 (dd, J = 15 and 14 Hz 1H), 1.8 (m, 2H), 2.0−2.1 (m, 2H), 2.26 (m, 2H), 2.5 (m, 2H), 2.6 (m, 1H), 3.35 (d, J = 7 Hz, 9H, PO*Me*), 3.60 (d, J = 9H, 1H), 4.91 (t, J = 7 Hz, 1H), 5.1 (m, 2H), 5.94 (t, J = 9 Hz, 1H). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): δ 169.1 (s). **4a**: ^1H NMR (300.4 MHz, C_6D_6): δ 1.7 (br, 1H, 8-CH_2), 2.0 (m, 1H, 8-CH_2), 2.1 (obscured by the signal due to **3a**, 7-CH_2) 2.4 (br, 1H, 7-CH_2), 3.3−3.4 (obscured by the signal due to PO*Me*, 1- and 4-C*H*), 5.1−5.3 (m, 3H, 2-, 3-, 6-C*H*), 6.34 (t, J = 9 Hz, 1H, 5-C*H*). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): δ 154 (br, 2P), 169 (br, 1P).

Reactions with P(OEt)$_3$. (a) Reaction of complex **1** (106.2 mg, 0.336 mmol) with $P(OEt)_3$ (162 μL, 0.846 mmol) in hexane

at 50 °C for 22 h followed by workup and recrystallization from pentane gave a white powder of Ru(6-η^1:1−3-η^3-COT){P(OEt)$_3$}$_3$ (**3b**) in 14% yield (32.4 mg, 0.046 mmol). The ^{1}H NMR spectrum of **3b** was characterized by use of ^{1}H−^{1}H COSY and ^{13}C−^{1}H shift correlation spectra. ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.11 (t, J = 8 Hz, 9H, POCH$_2$C*H*$_3$), 1.24 (t, J = 8 Hz, 9H, POCH$_2$C*H*$_3$), 1.26 (t, J = 8 Hz, 9H, POCH$_2$C*H*$_3$),1.98 (m, 1H, 7-C*H*$_2$), 2.18 (dt, J = 12, 8 Hz, 1H, 8-C*H*$_2$), 2.65 (m, 1H, 8-C*H*$_2$), 2.8 (m, 2H, 6-C*H* and 7-C*H*$_2$), 3.79 (dqui, J = 10, 7 Hz, 3H, POC*H*$_2$CH$_3$), 3.86 (dqui, J = 10, 7 Hz, 3H, POC*H*$_2$CH$_3$), 4.15 (m, 12H, POC*H*$_2$CH$_3$), 4.62 (m, 1H, 3-C*H*), 4.71 (dt, J = 14, 9 Hz, 1H, 2-C*H*), 4.86 (m, 1H, 1-C*H*), 5.77 (m, 1H, 5-C*H*), 5.88 (m, 1H, 4-C*H*). ^{13}C{^{1}H} (75.5 MHz, C_6D_6): δ 16.5 (d, J = 6 Hz, POCH$_2$*C*H$_3$), 16.6 (d, J = 6 Hz, POCH$_2$*C*H$_3$), 25.8 (dd, J = 7, 3 Hz, 8-*C*H$_2$), 43.7 (dt, J = 91, 11 Hz, 6-*C*H), 48.1 (dd, J = 8, 5 Hz, 7-*C*H$_2$), 59.2 (d, J = 5 Hz, POCH$_2$*C*H$_3$), 59.7 (d, J = 7 Hz, POCH$_2$*C*H$_3$), 59.8 (d, J = 5 Hz, POCH$_2$*C*H$_3$), 72.5 (d, J = 35 Hz, 3-*C*H), 76.8 (d, J = 32 Hz, 1-*C*H), 96.5 (s, 2-*C*H),127.2 (dd, J = 11, 6 Hz, 4-*C*H), 146.7 (dd, J = 10, 3 Hz, 5-*C*H). ^{31}P-{^{1}H} NMR (121.6 MHz, C_6D_6): δ 141.6 (t, J = 47 Hz, 1P, *apical-P*), 154.8 (dd, J = 47, 43 Hz, 1P, *equatorial-P*), 156.0 (dd, J = 47, 43 Hz, 1P, *equatorial-P*). HRMS (FAB): calcd for $C_{26}H_{55}O_9P_3Ru$ 706.21, found 706.4236. Anal. Calcd for $C_{26}H_{55}O_9P_3Ru$: C, 44.25; H, 7.86. Found: C, 44.02; H, 8.09.

(b) Complex **1** (22.7 mg, 0.0720 mmol) was reacted with P(OEt)$_3$ (40.0 μL, 0.233 mmol) in C_6D_6 and heated at 50 °C for 24 h. A mixture of complex **3b** and Ru(η^4-1,3,5-COT)-{P(OEt)$_3$}$_3$ (**4b**) was formed in 36% and 40% yields, respectively. Complex **4b** was characterized spectroscopically. **4b**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.1−1.3 (br, 27H, POCH$_2$C*H*$_3$), 1.2 (obscured by signals due to phosphite, 8-C*H*$_2$), 1.74 (br, 1H, 8-C*H*$_2$), 2.0 (m, 1H, 7-C*H*$_2$), 2.4 (br, 1H, 7-C*H*$_2$), 3.15 (t, J = 8 Hz, 1H, 4-C*H*), 3.26 (m, 1H, 1-C*H*), 3.8−4.2 (br, 18H, POC*H*$_2$-CH$_3$) 5.1−5.2 (m, 3H, 2-, 3-, 6-C*H*), 6.33 (t, J = 9 Hz, 1H, 5-C*H*).

Reaction with P(OMe)$_2$Ph. Complex **1** (22.6 mg, 0.0717 mmol) was reacted with P(OMe)$_2$Ph (36.0 μL, 0.227 mmol) in C_6D_6 and heated at 50 °C for 24 h. A mixture of Ru(η^4-1,5-COD)(η^4-1,3,5-COT){P(OMe)$_2$Ph} (**2c**), Ru(6-η^1:1−3-η^3-COT)-{P(OMe)$_2$Ph}$_3$ (**3c**), and Ru(η^4-1,3,5-COT){P(OMe)$_2$Ph}$_3$ (**4c**) was obtained in 30%, 13%, and 61% yields, respectively. These complexes were characterized spectroscopically, by use of ^{1}H−^{1}H COSY and analogy of the related complexes. **2c**: ^{1}H NMR-(300.4 MHz, C_6D_6): δ 0.87 (t, J = 14 Hz, 1H), 1.6 (br, 1H), 1.8 (br, 1H), 2.0 (br, 2H), 2.2 (obscured by signal due to free 1,5-COD), 2.37 (t, J = 8 Hz, 1H, 8-CH_2 in COT), 2.5 (m, 1H), 2.7 (m, 1H), 3.2−3.4 (obscured by signals due to **4c**, PO*Me*), 4.8 (obscured by signals due to **4c**, COT), 4.98 (m, 1H, COT), 5.10 (t, J = 8 Hz, 1H, COT), 5.2 (m, 1H, COT), 7.1−7.7 (m, 15H, P*Ph*). **3c**: ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 187.3 (s). **4c**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.19 (br t, J = 12 Hz, 1H, 8-C*H*$_2$), 1.4 (br, 1H, 8-C*H*$_2$), 1.8 (m, 1H, 7-C*H*$_2$) 2.1 (m, 1H, 7-C*H*$_2$), 2.84 (br, 1H, 4-C*H*), 3.0 (m, 1H, 1-C*H*), 3.2−3.4 (m, 18H, PO*Me*), 4.8−4.9 (m, 3H, 2-, 3-, 6-C*H*), 5.48 (t, J = 9 Hz, 1H, 5-C*H*), 7.1−7.7 (m, 15H, P*Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 174.0 (br, 1P), 174.4 (br, 1P), 189.4 (br, 1P).

Reaction with P(OEt)$_2$Ph. Reaction of complex **1** (21.2 mg, 0.0672 mmol) with P(OEt)$_2$Ph (40.0 μL, 0.208 mmol) in C_6D_6 at 50 °C for 24 h gave a mixture of Ru(6-η^1:1−3-η^3-COT)-{P(OEt)$_2$Ph}$_3$ (**3d**) and Ru(η^4-1,3,5-COT){P(OEt)$_2$Ph}$_3$ (**4d**) in 11% and 77% yields, respectively. These complexes were characterized spectroscopically by ^{1}H−^{1}H COSY and analogy of the related complexes. Since resonances due to **3d** in the ^{1}H NMR spectrum were significantly obscured by the signals due to **4d** and the yield of **3d** was low, complex **3d** was characterized by the ^{31}P{^{1}H} NMR spectrum. **3d**: ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 159.3 (t, J = 37 Hz, 1P, *apical-P*), 173.3 (dd, J = 37, 25 Hz, 1P, *equatorial-P*), 175.8 (dd, J = 37, 25 Hz, 1P, *apical-P*). **4d**: 0.25 (br t, J = 10 Hz, 1H, 8-CH_2), 1.2 (m, 18H, POCH$_2$*Me*), 1.3 (br, 1H, 8-C*H*$_2$), 1.75 (m, 1H, 7-C*H*$_2$), 2.1 (m, 1H, 7-C*H*$_2$), 2.8 (m, 1H, 4-C*H*), 2.95 (q, J = 7H, 1H, 1-C*H*), 3.5−4.0 (m, 12H, POC*H*$_2$Me), 4.8−5.0 (m, 3H, 2-, 3-, and 6-C*H*), 5.45 (t, J = 9 Hz, 1H, 5-C*H*), 7.15−7.25 (m, 12H, P*Ph*), 7.7−7.8 (m, 3H, P*Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 168.6 (br dd, 40, 18 Hz, 1P), 169.3 (br dd, J = 40, 18 Hz, 1P), 183.6 (br t, J = 18 Hz, 1P).

Reaction with P(O^{i}Pr)$_3$. Reaction of complex **1** (17.2 mg, 0.0545 mmol) with P(O^{i}Pr)$_3$ (40.0 μL, 0.162 mmol) in C_6D_6 at 50 °C for 20 h gave a mixture of Ru(6-η^1:1,3-η^3-COT){P(O^{i}Pr)$_3$}$_3$ (**3e**) and Ru(η^4-1,3,5-COT){P(O^{i}Pr)$_3$}$_3$ (**4e**) in 8% and 48% yields, respectively. These complexes were characterized spectroscopically by ^{1}H−^{1}H COSY and analogy of the related complexes. Since resonances due to **3e** in the ^{1}H NMR spectrum were significantly obscured by the signals due to **4e** and the yield of **3e** was low, complex **3e** failed to be characterized except the following resonances. **3e**: δ 4.4 (m, 3H, 1-, 2-, and 3-C*H*), 5.65 (m, 1H, 5-C*H*), 6.50 (dd, J = 12, 5 Hz, 1H, 4-C*H*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 138.7 (t, J = 43 Hz, *apical*-P), 153.0 (t, J = 43 Hz, *equatorial-P*), 157.2 (t, J = 43 Hz, *equatorial-P*). **4e**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.2−1.5 (m, 18H, POCH*Me*$_2$), 1.75 (br, 1H, 8-CH_2), 2.0−2.4 (br, 3H, 8- and 7-CH_2), 3.0 (br t, 1H, J = 5 Hz, 4-C*H*), 3.2 (br, 1H, 1-C*H*), 4.7−5.1 (br, 11H, POC*H*Me$_2$, 2- and 3-C*H*), 5.3 (m, 1H, 6-C*H*), 6.3 (t, J = 10 Hz, 1H, 5-C*H*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 147.9 (br d, J = 38 Hz, 2P), 161.4 (br t, J = 38 Hz, 1P).

Reaction with P(OMe)Ph$_2$. Reaction of complex **1** (21.3 mg, 0.0675 mmol) with P(OMe)Ph$_2$ (41.0 μL, 0.204 mmol) in C_6D_6 at 50 °C for 24 h gave a mixture of Ru(6-η^1:1−3-η^3-COT)-{P(OMe)Ph$_2$}$_3$ (**3f**) and Ru(η^4-1,3,5-COT){P(OMe)Ph$_2$} (**4f**) in 17% and 53% yields, respectively. These complexes were characterized spectroscopically by ^{1}H−^{1}H COSY and analogy of the related complexes. **3f**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.27 (br, 1H, 8-CH_2), 1.7 (br, 8-CH_2), 2.3 (obscured by impurity, 7-CH_2), 3.5 (m, 1H, 6-C*H*), 3.80 (br, 1H, 3-C*H*), 4.43 (dt, J = 17, 9 Hz, 1H, 2-C*H*), 4.6 (br, 1H, 1-C*H*), 5.05 (m, 1H, 5-C*H*), 5.27 (br, 1H, 4-C*H*), 6.9−7.7 (m, 30H, P*Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 126.6 (t, J = 29 Hz, 1P), 143.9 (t, J = 29 Hz, 1P), 144.8 (t, J = 29 H, 1P). **4f**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.7 (br t, J = 12 Hz, 8-CH_2), 1.5 (obscured by impurity, 8-CH_2), 1.78 (m, 1H, 7-CH_2), 2.0 (br, 1H, 7-CH_2), 2.6−3.0 (br, 11H, PO*Me*, 4-C*H*, and 1-C*H*), 4.30 (br, 1H, 2-C*H*), 4.54 (t, J = 8 Hz, 1H, 3-C*H*), 5.0 (m, 1H, 6-C*H*), 5.96 (t, J = 10 Hz, 1H, 5-C*H*), 6.9−7.7 (m, 30H, P*Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 140 (br, 2P), 152 (br, 1P).

Reactions with P(OEt)Ph$_2$. (a) Reaction of complex **1** (154.5 mg, 0.490 mmol) with P(OEt)Ph$_2$ (317.4 μL, 1.43 mmol) in toluene at 50 °C for 24 h followed by workup and recrystallization from a mixture of THF/hexane gave light yellow powders of Ru(η^4-1,3,5-COT){P(OEt)Ph$_2$}$_3$ (**4g**) in 42% yield (199.7 mg, 0.208 mmol). ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.6 (br, 1H, 8-CH_2), 0.9−1.3 (m, 10H, POCH$_2$*Me* and 8-CH_2), 1.9 (m, 1H, 7-CH_2), 2.2 (obscured by impurity, 7-CH_2), 2.7 (br, 2H, 1- and 4-C*H*), 2.9−3.4 (br, 6H, POCH_2Me), 4.30 (br, 1H, 2-C*H*), 4.45 (br t, J = 5 Hz, 1H, 3-C*H*), 5.0 (m, 1H, 6-C*H*), 5.95 (t, J = 10 Hz, 1H, 5-C*H*), 7.0−7.9 (m, obscured by impurity, *Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 164.0 (br, 2P), 174.8 (br, 1P).

(b) Reaction of **1** (8.9 mg, 0.028 mmol) with P(OEt)Ph$_2$ (18.3 μL, 0.0847 mmol) in benzene-d_6 (0.6 mL) at 50 °C gave Ru-(η^4-1,5-COD)(η^4-1,3,5-COT){P(OEt)Ph$_2$} (**2g**) in 89% within 10 min, and **2g** was then converted to a mixture of **3g** and **4g** in 16% and 52% yields, respectively, at 50 °C for 25 h. The ^{1}H NMR signals due to **3g** were significantly overlapped with signals of other complexes but estimated by COSY. **2g**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.87 (br, 1H, COT), 0.93 (t, J = 6 Hz, 3H, POCH$_2$*Me*), 1.5−2.5 (m, COD and COT, 13H), 2.6 (m, 1H, COT), 3.1 (m, 1H, COT), 3.2−3.5 (m, 4H, COD), 3.8 (obscured by free P(OEt)Ph$_2$, POCH_2Ph), 4.92 (t, J = 8 Hz, 2H, COT), 5.13 (t, J = 8 Hz, 1H, COT), 5.38 (t, J = 8 Hz, 1H, COT), 7.0−7.2 (obscured by free P(OEt)Ph$_2$), 7.59 (m, 4H, P*Ph*), 7.83 (t, J = 7 Hz, 2H, P*Ph*). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 151.4 (s, 1P). **3g**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.7 (7-CH_2),

1.9 (7-CH_2), 2.3 (6-C*H*), 3.4 (8-CH_2), 4.3 (br, 1H, 3-C*H*), 4.7 (t, J = 9 Hz, 1H, 2-C*H*), 4.9 (br, 1H, 1-C*H*), 5.6 (4- and 5-C*H*). ^{31}P NMR (121.6 MHz, C_6D_6): δ 149.3 (br, 1P), 167.9 (br, 2P).

Reactions with P(OPh)$_3$. (a) Complex **1** (171.5 mg, 0.544 mmol) was dissolved in hexane (4 mL) into which P(OPh)$_3$ (570.6 μL, 2.177 mmol) was added by a hypodermic syringe, and then the reaction mixture was stirred at 50 °C for 17 h, during which a white precipitate was deposited. The solvent was removed by a cannula, and the white precipitate was washed with cold hexane to give a 2:1 mixture of Ru(6-η^1:1−3-η^3-COT){P(OPh)$_3$}$_3$ (**3h**) and Ru(η^4-1,5-COD){P(OPh)$_3$}$_3$ (**5h**) (determined by ^{1}H NMR) as an analytically pure white powder in 3% yield (18.0 mg, 0.0158 mmol). The NMR spectrum was characterized by ^{1}H−^{1}H COSY and analogy of the related compounds. **3h**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.87 (dt, J = 12, 5 Hz, 1H, 7-CH_2), 1.51 (m, 1H, 8-CH_2), 2.2 (obscured by the signal due to **3c**, 8-CH_2), 2.78 (m, 1H, 7-CH_2), 3.28 (m, 1H, 6-C*H*), 4.3 (br, 1H, 3-C*H*), 4.7 (br, 1H, 1-C*H*), 4.95 (dt, J = 17, 8 Hz, 2-C*H*), 5.46 (br, 1H, 4-C*H*), 5.56 (m, 1H, 5-C*H*), 6.8−7.3 (m, obscured by the signals due to **5h**). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 127.8 (dd, J = 45, 44 Hz, 1P, *axial-P*), 144.0 (dd, J = 47, 45 Hz, 1P, *equatorial-P*), 146.2 (dd, J = 47, 44 Hz, 1P, *equatorial-P*). **5h**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 2.21 (br, 4H, CH_2 in COD), 2.35 (br, 4H, CH_2 in COD), 4.02 (br s, 4H, C*H*═ in COD), 6.8−7.3 (m, obscured by the signals due to **3h**). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 144.8 (s). Anal. Calcd for $C_{186}H_{167}O_{27}P_9Ru_3$ (as a 2:1 mixture of **3h** and **5h**): C, 65.39; H, 4.93. Found: C, 65.14; H, 4.73.

(b) Complex **1** (112.0 mg, 0.3551 mmol) was dissolved in hexane (5 mL) into which P(OPh)$_3$ (279.2 μL, 1.065 mmol) was added, and then the reaction mixture was warmed at 50 °C for 40 h. After removal of all volatile matters, the resulting white solid was recrystallized from a mixture of benzene/hexane (2 mL/1 mL), giving a white powder of Ru{P(OC$_6$H$_4$)-(OPh)$_2$}$_2${P(OPh)$_3$}$_2$ (**6h**) in 8% yield (36.8 mg, 0.0275 mmol). ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 6−9 (m, PO*Ph* and POC$_6H_4$). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$): δ 121.08 (ddd, J = 691, 62, 54 Hz, 1P, *axial-P*), 128.53 (ddd, J = 54, 42, 36 Hz, 1P, *equatorial-P*), 153.93 (ddd, J = 691, 54, 42 Hz, 1P, *axial-P*), 156.39 (ddd, J = 6, 54, 36 Hz, 1P, *equatorial-P*). Anal. Calcd for $C_{72}H_{58}O_{12}P_4Ru$: C, 64.52; H, 4.36. Found; 64.09; H, 4.42.

Reaction with P(OC$_6$H$_4$Cl-4)$_3$. Treatment of complex **1** (22.7 mg, 0.0720 mmol) with P(OC$_6$H$_4$Cl-4)$_3$ (115.5 mg, 0.2793 mmol) in benzene at 50 °C for 2.5 h followed by workup gave Ru{P(OC$_6$H$_3$Cl-4)(OC$_6$H$_4$Cl-4)$_2$}$_2${P(OC$_6$H$_4$Cl-4)$_3$}$_2$ (**6i**) in 41% yield (51.5 mg, 0.0294 mmol). ^{1}H NMR (300.4 MHz, C_6D_6): δ 6.5−7.0 (m, aromatic). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 121.7 (ddd, J = 690, 58, 54 Hz, 1P, *axial-P*), 129.2 (ddd, J = 54, 42, 36 Hz, 1P, *equatorial-P*), 154.4 (ddd, J = 690, 54, 42 Hz, 1P, *axial-P*), 156.7 (ddd, J = 58, 54, 36 Hz, 1P, *equatorial-P*).

Reactions with CN^{t}Bu. (a) An equimolar amount of *tert*-butylisonitrile (33.3 μL, 0.295 mmol) was added into a hexane solution (5 mL) of **1** (93.0 mg, 0.295 mmol), and the solution was stirred at room temperature for 2 h. All volatile materials were removed under vacuum, and the resulting solid was recrystallized from cold hexane to give pale yellow needles of Ru(η^4-1,5-COD)(η^4-1,3,5-COT)(CN^{t}Bu) (**2j**) in 26% yield (30.1 mg, 0.0755 mmol). Since quantitative formation of **2j** was shown by NMR study, the low yield is due to difficulty of manipulation. The ^{1}H NMR spectrum of **2j** was characterized by ^{1}H−^{1}H COSY and analogy of related complexes as well as elemental analysis. ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.22 (s, 9H, CN^t*Bu*), 1.38 (t, J = 12 Hz, 1H, 8-CH_2 in COT), 2.0−2.2 (m, 11H, 7- and 8-CH_2 in COT, CH_2 in COD), 2.36 (br t, J = 7 Hz, 1H, 4-C*H*), 2.4 (br, 1H, 1-C*H*), 2.6 (br m, 4H, CH_2 in COD), 3.19 (m, 1H, C*H* in COD), 3.52 (m, 1H, C*H* in COD), 5.02 (m, 2H, 2- and 3-C*H*), 5.13 (t, J = 6 Hz, 1H, 6-C*H*), 6.02 (dd, J = 6, 6 Hz, 1H, 5-C*H*). IR (KBr, cm^{-1}): 2120 (vs), 1641 (w). Anal. Calcd for $C_{21}H_{31}NRu$: C, 63.28; H, 7.84; N, 3.52. Found: C, 63.29; H, 8.10; N, 3.54.

(b) Treatment of **1** (91.3 mg, 0.289 mmol) with *tert*-butylisonitrile (100.0 μL, 0.884 mmol) in a Schlenk tube at 50 °C for 4 h followed by removal of volatile materials gave a white powder. Extraction of the white powder by hexane, which was stored in a deep freezer, led to crystallization of off-yellow crystals of Ru(η^4-1,5-COD)(CN^{t}Bu)$_3$ (**5j**) in 17% yield (22.4 mg, 0.0448 mmol). The ^{1}H NMR spectrum of **5j** was characterized by H−^{1}H COSY. ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.17 (s, 27H, CN^t*Bu*), 2.7 (m, 4H, *endo*- or *exo*-CH_2 in COD), 2.9 (m, 4H, *exo*- and *endo*-CH_2 in COD), 3.8 (m, 4H, ═C*H* in COD). ^{13}C-{^{1}H} NMR (75.5 MHz, C_6D_6): δ 31.3 (s, CMe_3), 35.4 (s, CH_2 in COD), 55.5 (s, CMe_3), 69.8 (s, *C*H in COD), 178.7 (s, *C*N^{t}Bu). IR (KBr, cm^{-1}): 2972 (w), 2923 (w), 2862 (w), 2796 (w), 2126 (vs), 2102 (vs), 1847 (vs), 1457 (m), 1364 (m), 1212 (s). Anal. Calcd for $C_{23}H_{39}N_3Ru$: C, 60,23; H, 8.57; N, 9.16. Found: C, 59.44; H, 8.83; N, 8.98.

(c) Complex **1** (18.3 mg, 0.0580 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) was introduced by bulb-to-bulb distillation. Three equivalents of *tert*-butylisonitrile (20.0 μL, 0.177 mmol) was added by a hypodermic syringe through the rubber septum. Quantitative formation of **2j** was confirmed by 15 min at room temperature by NMR spectrum. The reaction mixture was heated at 50 °C for 2.5 h to give **5j** in 58% yield, where liberation of 1,5-COD (10%) and 1,3,5-COT (38%) were observed. Further treatment of the reaction mixture at 50 °C for 23 h gave Ru(6-η^1:1−3-η^3-COT)(CN^{t}Bu)$_3$ (**3j**), where amounts of liberated 1,5-COD and 1,3,5-COT were estimated to be 92% and 25% yields, respectively, based on **1**. **3j**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 0.87 (s, 9H, *apical*-CN^t*Bu*), 1.19 (s, 9H, *equatorial*-CN^t*Bu*), 1.21 (s, 9H, *equatorial*-CN^t*Bu*), 2.2 (m, 2H, 7- and 8-CH_2), 2.7 (m, 1H, 6-C*H*). 2.8 (m, 2H, 7- and 8-CH_2), 4.59 (t, J = 7.5 Hz, 1H, 2-C*H*), 4.75 (dd, J = 8, 4 Hz, 1H, 3-C*H*), 4.96 (td, J = 8, 4 Hz, 1H, 1-C*H*), 5.92 (dd, J = 7, 4 Hz, 1H, 5-C*H*), 6.04 (dd, J = 7, 4 Hz, 1H, 4-C*H*).

(d) Complex **5j** (9.3 mg, 0.020 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) and then 2 equiv of 1,3,5-COT (5.2 μL, 0.041 mmol) were introduced. The reaction mixture was warmed at 50 °C, and the time courses of the reaction were periodically monitored by ^{1}H NMR. Complex **5j** completely disappeared by 7 h, and **3j** was produced in 54% yield.

(e) Isolated complex **5j** (8.8 mg, 0.028 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) and then 10 equiv excess of *tert*-butylisonitrile (31.5 μL, 0.279 mmol) were added. The reaction mixture was warmed at 70 °C for 2 days to give a light yellow solution of **7** in 55% yield with concomitant formation of 1,5-COD (91%) and unidentified precipitate. ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.21 (s).

(f) Complex **1** (92.5 mg 0.293 mmol) was dissolved in toluene (ca. 3 mL) into which *tert*-butylisonitrile (620 μL, 5.48 mmol) was added. The reaction mixture was stirred at 50 °C for 55 h, and then all volatile materials were removed under reduced pressure. The resulting solid was extracted with a mixture of acetone and hexane, and fractional crystallization of the solution gave light yellow crystals. Although instability of the crystals prevented a detailed analysis, it was characterized as a homoleptic isonitrile complex, Ru(CN^{t}Bu)$_5$ (**7**), on the basis of the following data, and the yield was estimated as 32% (48.0 mg, 0.0931 mmol). ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.21(s). IR (KBr, cm^{-1}): 2981 (m), 2937 (w), 2211 (sh), 2154 (vs), 2116 (s), 1637 (w), 1459 (w), 1372 (w), 1236 (sh), 1200 (m), 553 (m).

Reactions with CO. (a) Complex **1** (24.1 mg, 0.0716 mmol) was placed in an NMR tube into which C_6D_6 (0.6 mL) was introduced by bulb-to-bulb distillation. Then, CO (0.1 MPa) was introduced into the NMR tube. After 16 h at room temperature, Ru(η^4-1,5-COD)(η^4-1,3,5-COT)(CO) (**2k**) was obtained in 97% yield. Complex **2k** was characterized by analogy of related complexes. ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.47 (t, J = 8 Hz, 1H, 8-CH_2 in COT), 1.8−1.9 (m, 10H, 7-CH_2 in COT and CH_2 in COD), 2.3 (t, J = 8 Hz, 1H, 8-C*H* in COT), 2.4 (br

t, $J = 7$ Hz, 1H, 4-C*H* in COT), 2.6 (m, 1H, 1-C*H* in COT), 3.3 (m, 2H in COD), 3.7 (m, 2H, *CH* in COD), 4.81 (dd, $J = 7$, 6 Hz, 1H, 3-C*H* in COT), 4.96 (dd, $J = 7$, 6 Hz, 1H, 2-C*H* in COT), 5.07 (dt, $J = 11$, 7 Hz, 1H, 6-C*H* in COT), 6.12 (dd, $J = 11$, 8 Hz, 1H, 5-C*H* in COT). Complexes **3k** and **5k** were characterized spectroscopically by use of ^{1}H−^{1}H COSY and analogy of related compounds. **3k**: ^{1}H NMR (300.4 MHz, C_6D_6): δ 1.64 (td, $J = 8$, 6 Hz, 1H, 8-CH_2 in COT), 1.7 (m, 1H, 7-C*H* in COT), 1.9 (partly obscured by signals due to **5k**, 8-CH_2 in COT), 2.2 (obscured by signals due to **5k**, 7-CH_2), 2.7 (br, 1H, 7-CH_2 in COT), 3.87 (t, $J = 8$ Hz, 1H, 2-C*H* in COT), 4.57 (m, 1H, 3-C*H* in COT), 4.79 (td, $J = 8$, 5 Hz, 1-C*H* in COT), 5.29 (t, $J = 4$ Hz, 2H, 5- and 4-C*H* in COT). **5k**: ^{1}H (300.4 MHz, C_6D_6): δ 1.9 (m, 4H, CH_2 in COD), 2.1 (m, 4H, CH_2 in COD), 3.8 (m, 4H, *CH* in COD).

(b) Complex **1** (100 mg, 0.317 mmol) was placed in a 200 mL Schlenk tube into which hexane (ca. 4 mL) was added under nitrogen atmosphere. After evacuation of the system by freeze−pump−thaw cycles, CO (0.1 MPa) was introduced into the system and stirred at 50 °C for 20 days to give an orange precipitate of $Ru_3(CO)_{12}$ in 44% yield/Ru (30 mg, 0.047 mmol). IR (hexane, cm^{-1}): 2072 (s), 2061 (s), 2038 (s), 1995 (vs), 1960 (w).

Reaction with NEt$_3$. Complex **1** (14.2 mg, 0.045 mmol) was placed in an NMR tube into which benzene-d_6 (ca. 0.6 mL) was added by vacuum distillation. The NMR tube was capped with a rubber septum under nitrogen atmosphere, and then NEt_3 (19 μL, 0.14 mmol) was injected into the NMR tube by use of a hypodermic syringe. The reaction system was warmed at 50 °C for 3 days, during which the reaction course was periodically monitored by NMR. The NMR data show that complex **1** remained unreacted under these conditions. Similarly, neither pyridine nor DMAP reacted with **1** at all under these conditions.

X-ray Analysis of 5j. A selected crystal of complex **5j** obtained by recrystallization from cold acetone was mounted on top of a glass capillary by using paraton-N oil. The crystallographic data and experimental details are summarized in Table 3.

The measurement was made on a Rigaku RASA-7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a rotating anode generator. The reflection intensities were monitored by three standard reflections at every 150 measurements. No decay correction was applied. Reflection data were corrected by psi-scan methods. The structure was solved by direct methods, SIR92[36] full-matrix least-squares calculations. All atoms except hydrogen atoms were found and were solved anisotropically. These calculations were performed on a Silicon Graphics O_2 workstation using the program system teXsan.[37]

(35) (a) Cope, A. C.; Haven, A. C. Jr.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867. (b) *Organic Synthesis*; Vol. 73, p 240.

Table 3. Crystallographic and Physical Data for Ru(η^4-1,5-COD)(CN^{t}Bu)$_3$ (5j)

formula	$C_{23}H_{39}N_3Ru$
fw	458.65
cryst color	yellow
habit	prismatic
cryst size, mm	0.70 × 0.5 × 0.3
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a, Å	29.030(6)
b Å	9.726(6)
c, Å	19.438(6)
β, deg	116.96(2)
V, Å^3	4891(3)
Z	8
D(calcd), g cm^{-3}	1.25
data collection temp, *K*	200 ± 1
scan mode	$\omega-2\theta$
scan width, deg	1.73 + 30.30 tan θ
scan speed, deg min^{-1}	32.0
$2\theta_{max}$	55.0
no. of measd reflns[a]	6066
R_{int}	0.085
no. of obsd reflns[b]	3793
no. of params refined	245
reflection/param ratio	15.48
R[c]	0.070
R_w[c]	0.090
GOF[d]	0.90

[a] Total. [b] $I > 3.00\sigma(I)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$. [d] Goodness of fit.

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Supporting Information Available: Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles for **5j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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