Synthesis of Ruthenium Triazolato and Tetrazolato Complexes by 1,3-Dipolar Cycloadditions of Ruthenium Azido Complex with Alkynes and Alkenes and Regiospecific Alkylation of Triazolates

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The [3+2] cycloaddition reactions of alkynes and alkenes with ruthenium azido complex [Ru]-N_3 (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) have been investigated. The metal-bound heterocyclic complexes produced are triazolates [Ru]$N_3C_2(CO_2Me)_2$ (**2**) and [Ru]$N_3C_2HCO_2Me$ (**3**) from dimethyl acetylene dicarboxylate and methyl propiolate, respectively. Reaction of **1** with fumaronitrile in CH_2Cl_2 at room temperature results in removal of a HCN molecule and produces the triazolato complex [Ru]N_3C_2HCN (**4**). In contrast, reaction of tetracyanoethene with **1** affords the tetrazolato complex [Ru]$N_4C[C(CN){=}C(CN)_2]$ (**5**). The structures of these complexes are all clearly established as N(2)-bound. Alkylation of **2** with organic bromides causes cleavage of the Ru−N bond and affords [Ru]-Br and *N*(1)-alkylated five-membered-ring organic triazoles $N_3(R)C_2(CO_2Me)_2$ (**6a**, R = $CH_2C_6F_5$; **6b**, R = CH_2Ph; **6c**, R = CH_2CO_2Me). Reaction of **3** with excess methyl propiolate gives a mixture of *Z*- and *E*-form zwitterionic *N*(1)-bound *N*(3)-alkylated-4-substituted triazolato complexes [Ru]$N_3(CH{=}CHCO_2Me)C_2H(CO_2)$ (**7**) in a ratio of ca. 4:1. Reaction of (*Z*)-**7** with ICH_3 affords {[Ru]$N_3(CH{=}CHCO_2Me)C_2H(CO_2Me)$}[I] (**8a**) and the following cleavage of the Ru−N bond gives [Ru]-I and an organic triazole, $N_3(CH{=}CHCO_2Me)C_2H(CO_2Me)$ (**9a**). A regiospecific alkylation happens by treatment of **3** with organic halides and gives a series of cationic *N*(1)-bound *N*(3)-alkylated-4-substituted triazolato complexes exclusively with high yields. The structures of **2**, **3**, **4**, **5**, (*Z*)-**7**, and **10a** have been determined by single-crystal X-ray diffraction analysis.

Introduction

1,3-Dipolar cycloaddition[1−6] is a common process in organic chemistry. Among various 1,3-dipoles, organic azides[3,6] are particularly important for synthesizing heterocyclic compounds. By analogy, coordinated azide in metal complexes can also undergo cycloaddition.[7]Thus, azido complexes have been reported to react with nitriles[8−21] and isonitriles[9,22−25] to produce metal−nitrogen- and metal−carbon-bonded tetrazolates, respectively. Similar reactions with alkynes[8,13,17,19,20,26−28] produce triazolates; alkenes, however, react very slowly and mostly afford impure products.[8,19] Azido complexes

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react with carbon disulfide[8,9,13,15–17,29] to produce thiothiatriazolate. Several azido complexes have been found to react with organic isothiocyanates[8,15,19,20,30] and alkyl thiocyanates[13,19,20] to give tetrazolinethionates and 5-(thioalkyl)tetrazolates, respectively. A survey[8] of the azido complexes known to take part in cycloaddition reactions discloses that the metals involved are most often palladium(II),[31] platium(II),[16] or cobalt(III),[19,32] although a whole range of other transition metals[21,33–35] has been used. In this paper, we reported the [3+2] cycloaddition reactions of alkynes and alkenes with the ruthenium azido complex. The stable triazolato and tetrazolato products we obtained in all cases were *N*(2)-bound. A series of regiospecific alkylation of triazolato complexes occurred. It was hoped that this type of reaction could be developed into a high-yield synthetic procedure for the exclusive preparation of 1,4,5-trisubstituted and 3,4-disubstituted triazoles. This hope was partially realized. We successfully synthesized the 1,4,5-trisubstituted triazoles from the 4,5-disubstituted triazolate but the isolation failed. Alkylation of the 4-substituted triazolates does proceed in high yield with the exclusive formation of *N*(1)-bound 3,4-disubstituted triazolates. We now disclose the results of detailed synthetic and structural investigations herein.

Results and Discussion

Preparation of the Azido Complex. Treatment of [Ru]-Cl ([Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) with NaN_3 in ethanol at reflux for 4 h affords the orange-yellow product [Ru]-N_3 (**1**) with an isolated yield of 99%. The ^{31}P NMR spectrum of **1** displays a singlet resonance at δ 81.5 assigned to the dppe ligand. The ^{1}H NMR spectrum of **1** displays a singlet resonance at δ 4.47, which is assigned to Cp. Complex **1** is soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, and acetone, moderately soluble in diethyl ether, and stable in solution and in the air.

Reaction of 1 with Dimethyl Acetylene Dicarboxylate. Treatment of complex **1** with a 5-fold excess of dimethyl acetylene dicarboxylate in CH_2Cl_2 at room temperature for 24 h affords the *N*(2)-bound 4,5-bis(methoxycarbonyl)-1,2,3-triazolato complex [Ru]$N_3C_2(CO_2Me)_2$ (**2**) with 90% isolated yield. The structure of **2** is clearly established as the *N*(2)-bound isomer from the appearance of its ^{1}H NMR spectrum ,which shows a singlet at δ 3.62 for the six methoxycarbonyl protons. The ^{1}H NMR spectrum of a *N*(1)-bound isomer would exhibit two resonances for its anisochronous methoxycarbonyl groups. The ^{31}P NMR resonance of **2** appears at δ 87.3. The FAB mass spectrum displays a parent peak at *m*/*z* 749.2 (M^+). In a previous study, the triazole and tetrazole anion could be coordinated by a metal center through either its *N*(1) or *N*(2) nitrogen atom.[8] Molecular orbital calculations[36–38] indicate that these two bonding modes are essentially isoenergetic. Evidence obtained to date indicates that either two isomers *N*(1) and *N*(2) are formed simultaneously[8,13,19,20,36–38] or only the *N*(2) isomer is produced exclusively.[8,13,19,20] In our case, the *N*(2)-bound isomer is produced exclusively.

Surprisingly, the reaction of **1** with either dimethyl fumarate or dimethyl maleate gives **2**, identical with the reaction of **1** with dimethyl acetylene dicarboxylate. The yields of the reactions are 91% and 90%, respectively. The reaction is completed in one week at room temperature. In both reactions, complex **2** is formed by [3+2] cyclization between the azido ligand and a C=C double bond following removal of a H_2 molecule. There are a few examples of cycloaddition of alkenes to coordinated azides,[8,19,39] but most of the alkenes investigated did not produce pure products and the triazolinates produced were generally thermally unstable and base sensitive. Generally, these reactions occur over a long period of time as with the corresponding alkyne reactions.[19] To our knowledge, this is the first example that cycloaddition of alkenes with the ruthenium azido complex via removal of one molecule yields a thermally stable, pure, and high-yield triazolato product. The structure of **2** produced from dimethyl fumarate is determined to establish the geometry and the bonding mode about the triazolato ligand. Complex **2** was characterized by a single-crystal X-ray diffraction analysis; an ORTEP drawing is shown in Figure 1. Crystal and intensity collection data are given in Table 1. Selected bond distances and bond angles are given in Table 2. The triazolato ligand is *N*(2)-bound to ruthenium and the five atoms of the triazolato ring are essentially planar.

Reaction of 1 with Methyl Propiolate. Treatment of complex **1** with a 5-fold excess of methyl propiolate in CH_2Cl_2 at room temperature for 8 h affords the *N*(2)-bound 4-methoxycarbonyl-1,2,3-triazolato complex, [Ru]-$N_3C_2HCO_2Me$ (**3**), with 73% isolated yield. By monitoring the reaction with ^{31}P NMR spectroscopy, two singlet resonances at δ 88.40 and 88.20 attributed to the *N*(1)- and *N*(2)-bound isomers, respectively, were observed at the initial stage of the reaction. The *N*(1)-bound isomer, in hours at room temperature, converted to the *N*(2)-bound isomer. The molecular structure of **3** was determined by an X-ray diffraction study; an ORTEP drawing is shown in Figure 2 and selected bond distances and bond angles are given in Table 1. The triazolato ligand is *N*(2)-bound. The five-membered triazolato ring exhibits an irregular pentagonal structure and is essentially planar.

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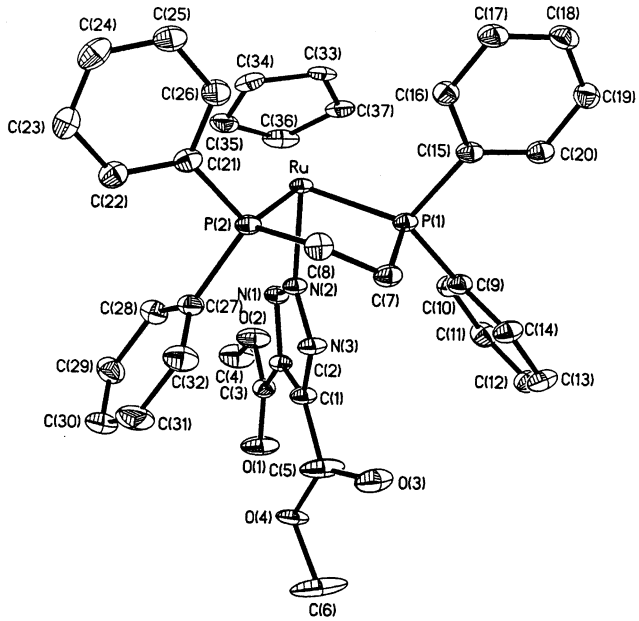


Figure 1. ORTEP drawing of **2**; thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2, 3, and 4

	2	3	4
Ru−N2	2.090(2)	2.085(2)	2.0990(18)
N1−N2	1.331(3)	1.352(3)	1.340(3)
N2−N3	1.332(3)	1.336(3)	1.325(3)
N3−C1	1.351(3)	1.359(3)	1.355(3)
N1−C2	1.352(3)	1.337(3)	1.331(3)
C1−C2	1.400(4)	1.382(4)	1.367(4)
P1−Ru−P2	85.13(3)	83.60(3)	83.88(3)
N2−Ru−P1	86.48(6)	90.78(7)	86.80(6)
N2−Ru−P2	89.89(6)	89.67(6)	90.16(5)
Ru−N2−N1	121.4(2)	124.81(17)	124.09(15)
Ru−N2−N3	125.2(2)	122.31(18)	123.14(14)
N2−N3−C1	105.5(2)	104.8(2)	104.7(2)
N1−N2−N3	113.4(2)	112.8(2)	112.64(18)
N2−N1−C2	105.6(2)	105.3(2)	105.7(2)
N3−C1−C2	107.8(2)	108.5(2)	108.6(2)
N1−C2−C1	107.7(2)	108.6(3)	108.2(2)

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5

Ru−P1	2.2768(5)	Ru−P2	2.2927(5)
Ru−N2	2.0702(16)	N1−N2	1.328(2)
N2−N3	1.356(2)	N1−C1	1.351(3)
N3−N4	1.312(3)	N4−C1	1.342(3)
N5−C4	1.130(4)	N6−C5	1.148(4)
N7−C6	1.139(3)	C1−C2	1.438(3)
C2−C3	1.303(4)	C2−C4	1.530(4)
C3−C6	1.391(4)	C3−C5	1.501(4)
P1−Ru−P2	84.103(19)	N2−Ru−P1	91.04(5)
N2−Ru−P2	88.13(5)	Ru−N2−N1	128.70(13)
Ru−N2−N3	119.45(13)	N2−N1−C1	102.37(18)
N2−N3−N4	108.41(18)	N3−N4−C1	104.99(18)
N4−C1−N1	113.14(19)	N4−C1−C2	119.2(2)
N1−C1−C2	127.6(2)	C1−C2−C3	127.6(3)
C3−C2−C4	118.1(2)	C1−C2−C4	114.3(2)
C2−C3−C6	123.9(3)	C2−C3−C5	118.9(3)
C6−C3−C5	117.1(3)		

Reaction of 1 with Fumaronitrile. Treatment of **1** with fumaronitrile at room temperature for 12 h affords the *N*(2)-bound 4-cyano-1,2,3-triazolato complex, $[Ru]N_3C_2HCN$ (**4**), with 80% isolated yield. The ^1H NMR spectrum of **4** displays a characteristic singlet resonance at δ 7.03 assigned to CH and a singlet resonance at δ 4.58 attributed to Cp. The ^{31}P NMR resonance of **4** appears at δ 88.2. In the ^{13}C NMR, a resonance at δ 119.1 is assigned to CN. The FAB mass spectrum displays a parent peak at *m*/*z* 658.2 (M^+). In principle, the cycloaddition of fumaronitrile to coordinated azide can take place via C=C or C≡N. The reaction of coordinated azide in Ni(II) with CH_2=CHCN gave a triazolinato complex.[8] A pathway via direct cyclization of HC≡CCN with azide resulting in the formation of triazolate also occurred.[39b] The product **4** is clearly established to be formed by [3+2] cyclization between the azido ligand and a C=C double bond following removal of a HCN molecule. The structure of **4** was determined by an X-ray diffraction study; an ORTEP drawing is shown in Figure 3 and selected bond distances and bond angles are given in Table 1. The coordination geometry is very similar to that of **3**. As observed, the triazolato ring is *N*(2)-bound. The bond distances of the triazolato ring are similar to but a little

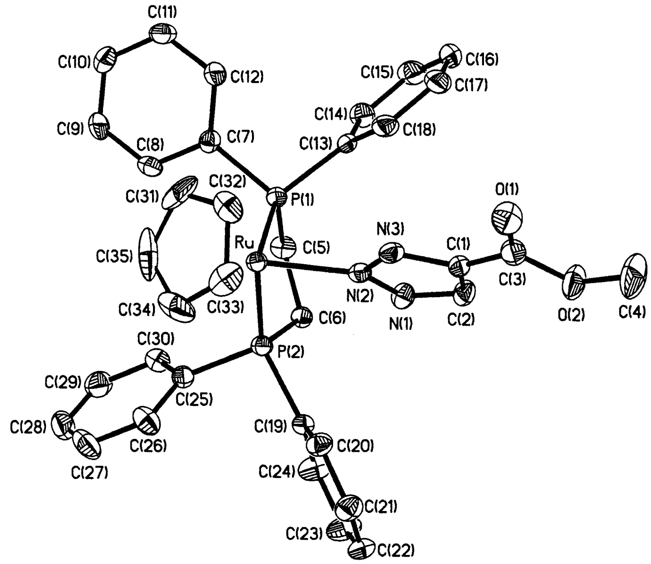


Figure 2. ORTEP drawing of **3**; thermal ellipsoids are drawn at the 50% probability level.

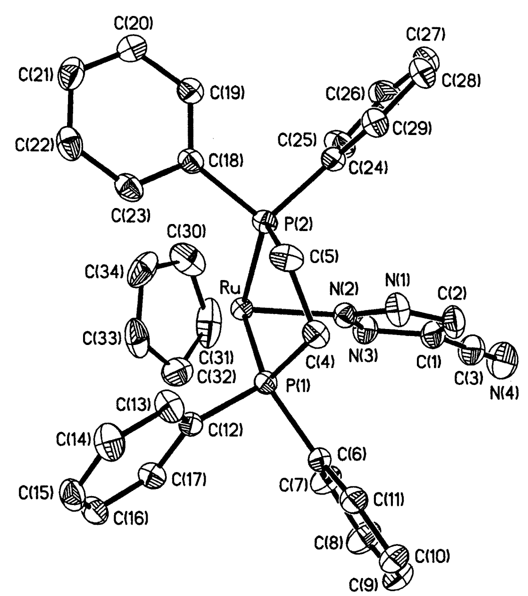
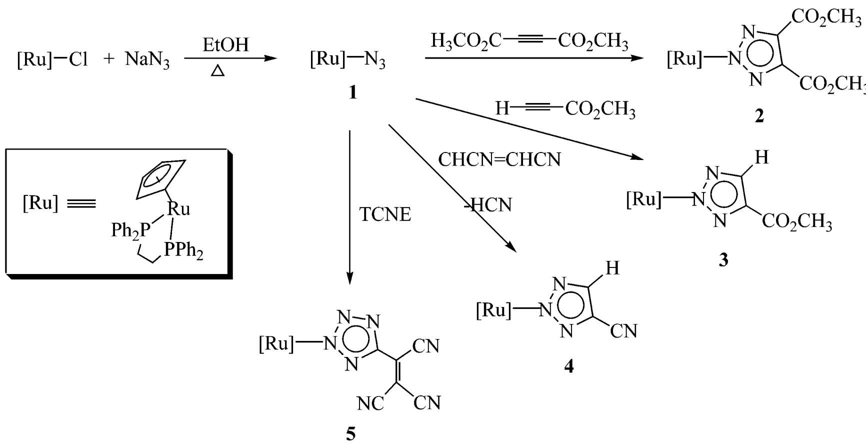


Figure 3. ORTEP drawing of **4**; thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



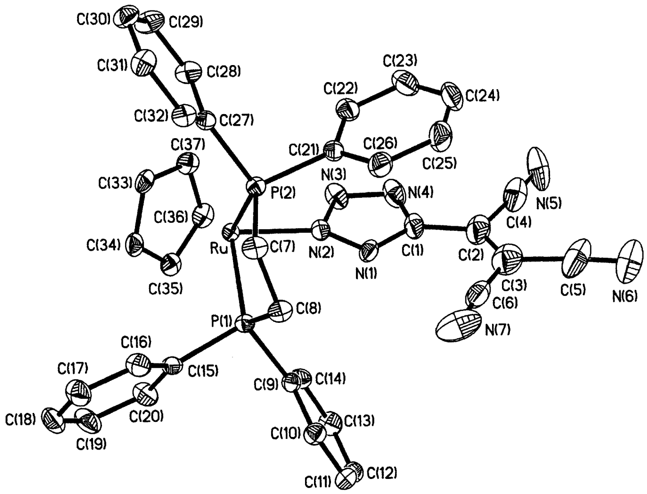


Figure 4. ORTEP drawing of **5**; thermal ellipsoids are drawn at the 50% probability level.

less than those of **3**. Therefore, the bonding mode is the same as **3** and the triazolate ring of **4** is marginally smaller.

Reaction of 1 with TCNE. The reaction of **1** with tetracyanoethene (TCNE) at room temperature for 24 h affords the tetrazolato complex $[Ru]N_4C[C(CN)=C(CN)_2]$ (**5**) with 80% isolated yield. The cycloaddition of $C(CN)_2=C(CN)_2$ to coordinated azide can take place via C=C or C≡N. That the product **5** is obtained when C≡N adds to coordinated azide is established by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 4 and selected bond distances and bond angles are given in Table 2. The planar five-membered tetrazolato ring is coordinated to the Ru center via the *N*(2) atom. Although the variation in bond distances is larger than those of triazolates, the bonding mode of this tetrazolate is probably best described as a π-delocalized bond in this five-membered ring. Reactivity of the reaction is highly related to the nature of the nitrile. Benzonitrile, acetonitrile, CF_3CN, and $HPhC=C(CN)_2$ do not react with complex **1** even under vigorous conditions. Recently we reported an interesting reaction of pentamethylcyclopentadienyl dppp (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) ruthenium azido complex with ICH_2CN affording an *N*-coordinated iodoacetonitrile complex.[40]

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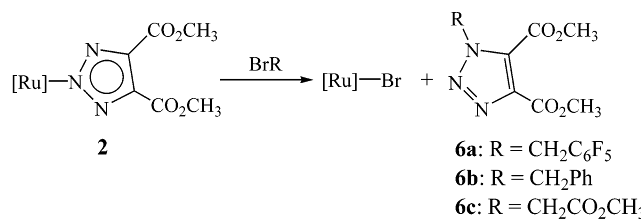
Scheme 2



Apparently, not only the steric effect but also the inductive effect should be considered as important driving forces for the reaction. Typically, tetrazoles are prepared from the corresponding nitriles by reaction with a hydrazoic source (e.g., sodium azide and ammonium chloride).[41−43] Alternative strategies, involving different azide anion sources such as trimethylsilyl azide in the presence of dialkyltin oxide,[44] have been developed for the conversion of amides into 1,5-disubstituted tetrazoles.[45,46] In addition, reaction of a cyano-substituted cyclopropenyl complex with trimethylsilyl azide reportedly gave a tetrazolato complex.[47]

Reactions of Triazolato Complexes with Electrophiles. Alkylation of **2** with a 10-fold excess of $BrCH_2C_6F_5$ in $CHCl_3$ at room temperature for one week causes cleavage of the Ru−N bond and affords [Ru]-Br and a *N*(1)-alkylated five-membered-ring organic triazole $N_3(CH_2C_6F_5)C_2(CO_2Me)_2$ (**6a**) (Scheme 2). At 50 °C and with a 20-fold excess of $BrCH_2C_6F_5$, the reaction is completed in 1 day. The alkylation is monitored by NMR spectroscopy. In the ^{31}P NMR spectrum, the resonance of **2** at δ 87.25 disappeared and the resonance at δ 79.86 attributed to [Ru]-Br appeared. In the ^1H NMR spectrum a singlet resonance appears at δ 4.56 attributed to Cp of [Ru]-Br and two singlet resonances appear at δ 3.98 and 3.88 attributed to two anisochronous methoxycarbonyl groups of **6a**. The FAB mass spectrum of the crude mixture displayed parent peaks at *m*/*z* 646.1 and 366.1 attributed to [Ru]-Br and **6a**, respectively. Similar reaction of **2** with other organic bromides gives

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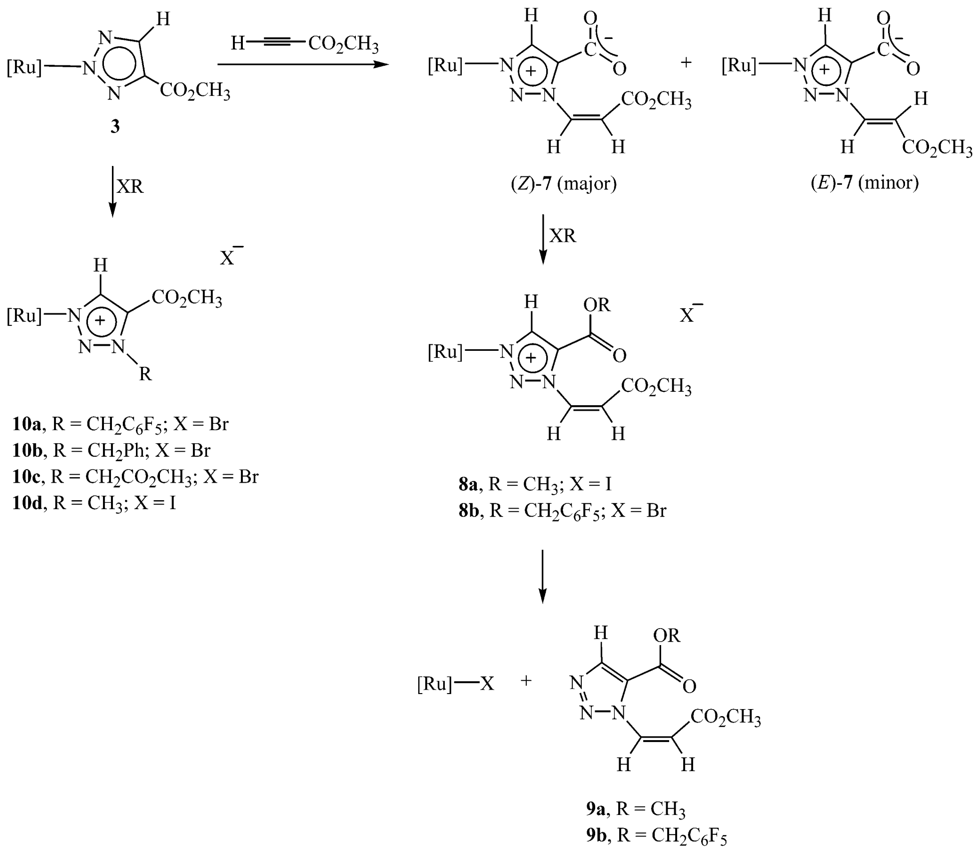
Scheme 3



[Ru]-Br and *N*(1)-alkylated five-membered-ring organic triazoles $N_3(R)C_2(CO_2Me)_2$ (**6b**, R = CH_2Ph; **6c**, R = $CH_2CO_2CH_3$) (Scheme 2). The structures of these free triazoles are clearly established as *N*(1)-alkylated from the appearance of their ^{1}H NMR spectra which exhibit two proton resonances for their anisochronous methoxycarbonyl groups. [Ru]-Br is easily isolated as a precipitate in *n*-pentane solution but the free triazoles **6a**−**c**, which mix with excess organic halides in *n*-pentane, are hard to isolated. Most attempts at isolating the triazole from the mixture have been unsuccessful. An alkylation of triazolato cobalt chelate complexes was made by Nelson and co-workers,[19] but isolation of the free triazole was not successful either. Noticeably, there is no reaction between organic iodides with **2**. Treatment of **2** with $HCl_{(aq)}$ causes a hydrolysis and no Ru−N bond-breaking is observed.

Reaction of 3 with Methyl Propiolate. Upon letting the $CHCl_3$ solution of **3** with excess methyl propiolate stand at room temperature for days, a mixture of the *Z*- and *E*-form zwitterionic triazolato complex $[Ru]N_3(CH{=}CHCO_2Me)C_2H(CO_2)$ (**7**) was obtained in a ratio of ca. 4:1 (observed by ^{1}H NMR spectroscopy after isolation) (Scheme 3). The reaction was monitored by ^{31}P NMR and ^{1}H NMR. After treatment of **3** with excess methyl propiolate in $CDCl_3$ for days, the ^{31}P NMR spectrum showed two signals appearing at δ 86.16 and 85.76 in a ratio of ca. 4:1 attributed to (*Z*)-**7** and (*E*)-**7**, respectively. In the ^{1}H NMR spectrum, two sets of AX pattern resonances appearing at δ 7.57, 5.42 (d, J_{H-H} = 10.31 Hz) and δ 8.65, 4.95 (d, J_{H-H} = 14.32 Hz) in a ratio of ca. 4:1 are assigned to the two vinyl protons of (*Z*)-**7** and (*E*)-**7**, respectively. The same reaction is observed in CD_3CN and *d*-acetone. Complex **7** is possibly formed by adding a methyl propiolate molecule to the hydrolyzed **3**. The purification of (*Z*)-**7** was achieved by washing (*E*)-**7** away with diethyl ether three times. The molecular structure of (*Z*)-**7** was determined by an X-ray diffraction study; an ORTEP drawing is shown in Figure 5 and selected bond distances and bond angles are given in Table 3. The triazolato ligand is *N*(1)-bound. The five-membered triazolato ring exhibits an irregular pentagonal structure and is essentially planar. The O1−C3 and O2−C3 distances of 1.250(6) and 1.249(7) Å, respectively, are both between the C−O double bond and the single bond,

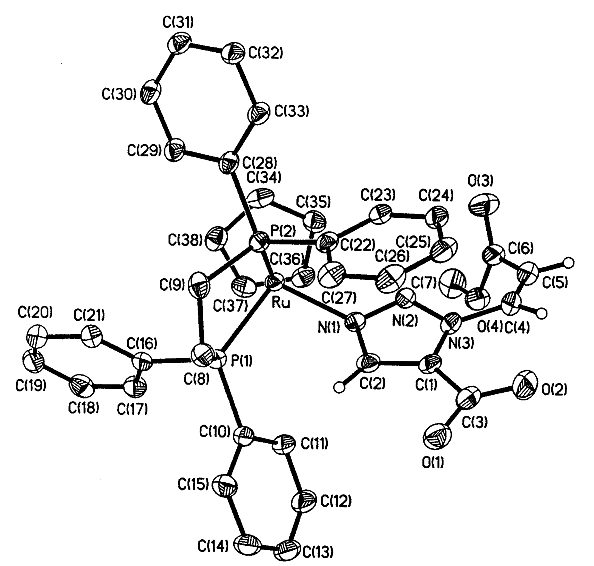


Figure 5. ORTEP drawing of (*Z*)-**7**; thermal ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (*Z*)-7

Ru−P1	2.2831(12)	Ru−P2	2.2893(12)
Ru−N1	2.108(4)	N2−N3	1.344(5)
N1−N2	1.327(5)	N3−C1	1.362(6)
N1−C2	1.362(6)	C1−C2	1.363(7)
C1−C3	1.522(7)	C4−C5	1.316(7)
C5−C6	1.462(8)	O1−C3	1.250(6)
O2−C3	1.249(7)	O3−C6	1.203(6)
O4−C6	1.341(7)	O4−C7	1.441(7)
P1−Ru−P2	83.78(4)	N1−Ru−P1	93.58(10)
N1−Ru−P2	89.47(10)	Ru−N1−N2	117.6(3)
Ru−N1−C2	131.8(3)	N1−N2−N3	106.3(2)
N2−N3−C1	111.2(4)	C2−N1−N2	109.4(4)
N3−C1−C2	104.7(4)	N3−C1−C3	126.8(4)
C2−C1−C3	128.1(4)	N1−C2−C1	108.3(4)
O1−C3−O2	128.5(5)	O1−C3−C1	113.7(5)
O2−C3−C1	117.7(5)	N3−C4−C5	125.7(5)
C4−C5−C6	130.0(5)		

indicating the delocalized π-bonding mode. The N3−C4−C5 and C4−C5−C6 angles of 125.7(5)° and 130.0(5)°, respectively, are larger than that of a typical C(sp^2) hybridization, possibly resulting from the steric crowding of the two substitutes in the *Z* conformation.

Reaction of (*Z*)-7 with Electrophiles. Treatment of (*Z*)-**7** with ICH_3 at room temperature for 24 h gives (*Z*)-{[Ru]N_3(CH=CHCO$_2$Me)C_2H(CO$_2$CH$_3$)}[I] (**8a**) with 90% isolated yield. Letting the $CHCl_3$ solution of (*Z*)-**7** and a 10-fold excess of ICH_3 stand at room temperature for 4 days causes cleavage of the Ru−N bond and gives [Ru]-I and an organic triazole, (*Z*)-N_3(CH=CHCO$_2$Me)-C_2H(CO$_2$Me) (**9a**). The excess CH_3I and CH_2Cl_2 were removed under vacuum. [Ru]-I and **9a** were separated by extracting the residue with *n*-pentane. The organic product **9a** was identified by high-resolution mass spectroscopy. The reaction of (*Z*)-**7** with $BrCH_2C_6F_5$ is similar to that of CH_3I, giving (*Z*)-{[Ru]N_3(CH=CHCO$_2$Me)C_2H(CO$_2$CH$_2$C$_6$F$_5$)}[Br] (**8b**) in 20 h at room temperature, and the following Ru−N bond cleavage gives [Ru]-Br and an organic triazole, (*Z*)-N_3(CH=CHCO$_2$Me)-C_2H(CO$_2$CH$_2$C$_6$F$_5$) (**9b**). [Ru]-Br is easily isolated as precipitate in *n*-pentane solution but the organic product **9b**, which mixed with excess organic halides in *n*-pentane, is hard to isolate.

Treatment of complex **3** with a 5-fold excess of $BrCH_2C_6F_5$ at room temperature for 12 h yields exclusively an alkylated product {[Ru]N_3(CH$_2$C$_6$F$_5$)C_2HCO$_2$Me}[Br] (**10a**) with 92% isolated yield (Scheme 3). For the *N*(2)-bound triazolato complex **3**, the alkylation might have occurred at one of two nitrogens, the N(1) nitrogen with less steric hindrance or the N(3) nitrogen with the more nucleophilicity. From the NMR spectra it is hard to determine the absolute structure of **10a**. To make crystals suitable for single-crystal X-ray diffraction analysis, we changed the counteranion Br^- to BF_4^-. Finally, the structure of **10a** was confirmed to be a *N*(1)-bound *N*(3)-alkylated-4-methoxycarbonyl triazolate by an X-ray diffraction analysis. The alkylation occurred at the more nucleophilic *N*(3) nitrogen atom and transformed to a less steric hindered *N*(1)-bound structure at the same time. Some regiospecific alkylations of triazoles and tetrazoles have been reported,[19,47,48] but to our knowledge such an alkylation of triazolates is the first example ever seen. Similar reactions of **3** with other organic halides also give exclusively cationic *N*(1)-bound *N*(3)-alkylated-4-methoxycarbonyl triazolato complexes {[Ru]N_3(R)C_2HCO$_2$Me}[Br] (**10b**, R = CH$_2$-Ph, X = Br; **10c**, R = CH$_2$CO$_2$Me, X = Br; **10d**, R = CH$_3$, X = I) with high yields (Scheme 3). Complexes **10a**−**d** are stable in $CHCl_3$ solution with excess organic bromides and no further Ru−N bond breaking was observed at room temperature or at reflux. An ORTEP drawing of **10a** is shown in Figure 6, and selected bond distances and bond angles are given in Table 4. The *N*(3)-alkylated triazolato ligand is *N*(1)-bound.

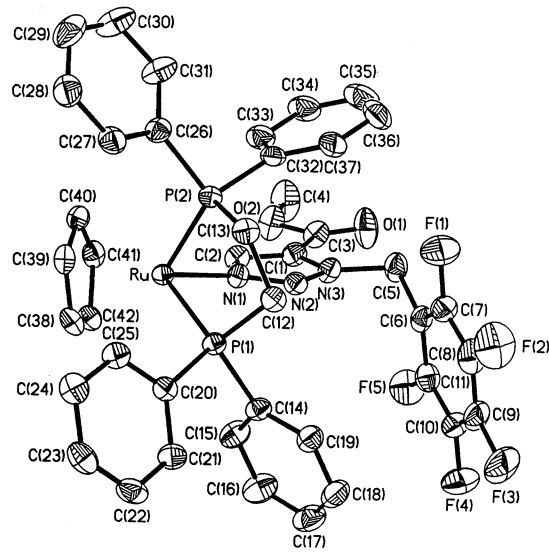


Figure 6. ORTEP drawing of **10a**; thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 10a

Ru−P1	2.2896(8)	Ru−P2	2.2863(8)
Ru−N1	2.106(3)	N2−N3	1.335(4)
N1−N2	1.329(4)	N3−C1	1.355(4)
N1−C2	1.354(4)	C1−C2	1.368(5)
C1−C3	1.480(5)	O1−C3	1.197(4)
O2−C3	1.326(4)	N3−C5	1.478(4)
P1−Ru−P2	84.51(3)	N1−Ru−P1	90.36(7)
N1−Ru−P2	89.58(7)	Ru−N1−N2	123.3(2)
Ru−N1−C2	126.7(2)	N1−N2−N3	106.9(2)
N2−N3−C1	111.0(3)	C2−N1−N2	108.9(3)
N3−C1−C2	104.7(3)	N3−C1−C3	125.0(3)
C2−C1−C3	130.1(3)	N1−C2−C1	108.4(3)
O1−C3−O2	125.2(5)	O1−C3−C1	125.9(3)
O2−C3−C1	108.9(3)	N3−C5−C6	111.6(3)

The alkylation of **4** is complicated. Treatment of **4** with organic halides at room temperature yields several alkylated products and [Ru]-Br is also observed in low yield. It shows that the alkylation of **4** is not regiospecific and the following Ru−N bond breaking happens. However, the attempt at isolating the products was not successful. In contrast to the facile alkylation of complex **4**, it is surprising that there is no reaction between complex **5** and electrophiles, which probably results from the steric and electronic influences of the substituent at the tetrazolato ring.

Conclusions

The reaction of ruthenium azido complex [Ru]-N_3 (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) and alkynes or alkenes with electron-withdrawing sub-

(48) Takash, N. E.; Holt, E. M.; Alcock, N. W.; Henry, R. A.; Nelson, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 2968.

stituents yielded a series of addition products via a [3+2] cycloaddition of a C≡C or C=C bond with the azido group. However, addition of a TCNE molecule to **1** resulted in a [3+2] cycloaddition via the C≡N and azido group and afforded a tetrazolato product. Complete characterization of these triazolato and tetrazolato complexes elucidates the structures and establishes the *N*(2)-bounding type of the addition products.

Reaction of the 4,5-disubstituted 1,2,3-triazolato complex **2** with organic bromides gave [Ru]-Br and a series of 1,4,5-trisubstituted organic triazoles, $N_3(R)C_2(CO_2Me)_2$ (**6a**, R = $CH_2C_6F_5$; **6b**, R = CH_2Ph; **6c**, R = $CH_2CO_2CH_3$). The 4-methoxycarbonyl-1,2,3-triazolato complex **3** reacts with excess methyl propiolate to give a mixture of *Z* and *E* form zwitterionic triazolato complex $[Ru]N_3(CH{=}CHCO_2Me)C_2H(CO_2)$ (**7**) in a ratio of 4:1. An organic triazole, (*Z*)-$N_3(CH{=}CHCO_2Me)C_2H(CO_2Me)$, is successfully synthesized by reaction of (*Z*)-**7** with ICH_3. A regiospecific alkylation of **3** with organic halides yields a series of cationic *N*(1)-bound 3,4-disubstituted ruthenium triazolato complexes exclusively with high yields. The steric influences of [3+2] cycloaddition by using the ruthenium center with different phosphine ligand are currently under investigation. A new method of synthesis will be developed by removing the heterocyclic five-membered-ring triazolato and tetrazolato ligands of ruthenium complexes, thus form a catalytic cycle.

Experimental Section

General Procedures. All manipulations were performed under nitrogen with use of vacuum-line, drybox, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 and diethyl ether and THF from sodium diphenyketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on an AM-300WB FT-NMR spectrometer at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as an initial standard ($CDCl_3$, δ 7.24: acetone-d_6, δ 2.04). IR spectra were measured on a Perkin-Elmer 983 instrument and referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Cp(dppe)RuCl complexes were prepared following the methods reported in the literature.[49] Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Synthesis of Cp(dppe)Ru-N_3 (1). To a Schlenk flask charged with Cp(dppe)RuCl (3.03 g, 5.05 mmol) and NaN_3 (1.97 g, 30.3 mmol) was added ethanol (50 mL). The resulting solution was heated to reflux for 4 h and cooled to room temperature. The solvent was dried under vacuum and 20 mL of CH_2Cl_2 was added to the residue. The product was dissolved in CH_2Cl_2 and other salts such as NaN_3 and NaCl precipitated. After filtration, the solvent was dried under vacuum to give the product Cp(dppe)RuN_3 (**1**; 3.03 g, 4.99 mmol, 99% yield). Spectroscopic data for **1** are as follows: IR (KBr, cm^{-1}) $\nu(N_3)$ 2018 (vs). ^1H NMR ($CDCl_3$) δ 7.82−7.18 (m, 20H, Ph), 4.47 (Cp), 2.80−2.30 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 81.52. ^{13}C NMR ($CDCl_3$) δ 133.6−127.9 (Ph), 79.9 (Cp), 27.7 (t, PCH_2, J_{C-P} = 22.4 Hz). MS (*m*/*z*, Ru^{102}) 607.3 (M^+), 579.2 ($M^+ - N_2$), 565.2 ($M^+ - N_3$). Anal. Calcd for $C_{31}H_{29}N_3P_2Ru$: C, 61.38; H, 4.82; N, 6.93. Found: C, 61.83; H, 4.91; N, 6.82.

Synthesis of *N*(2)-Bound Cp(dppe)Ru$N_3C_2(CO_2Me)_2$ (2). To a Schlenk flask charged with **1** (222.1 mg, 0.367 mmol) were added dimethyl acetylene dicarboxylate (234 mg, 1.65 mmol) and CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 24 h then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of *n*-hexane, giving a yellow precipitate. After filtration, the precipitate was washed with 2 × 10 mL of *n*-hexane and dried under vacuum to give the *N*(2)-bound Cp(dppe)Ru$N_3C_2(CO_2Me)_2$ (**2**) (245.8 mg, 0.329 mmol, 90% yield). The same product was formed by reaction of **1** (99.8 mg, 0.165 mmol) with dimethyl fumarate (118.9 mg, 0.825 mmol) at room temperature for one week. The yield was 91% (111.9 mg, 0.150 mmol). Spectroscopic data for **2** are as follows: IR (KBr, cm^{-1}) ν(C=O) 1737 (s), 1718 (vs), ν(N=N) 1438 (s), ν(C−O) 1285 (m). ^1H NMR ($CDCl_3$) δ 7.44−7.11 (m, 20H, Ph), 4.63 (Cp), 3.62 (s, 6H, $2CH_3$), 3.40−3.10, 2.70−2.40 (2m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 87.25. ^{13}C NMR (CDCl3) δ 161.9 (CO_2), 138.4 ($C(CO_2CH_3)$), 134.2−127.6 (Ph), 81.8 (Cp), 51.3 (OCH_3), 28.6 (t, PCH_2, J_{C-P} = 21.8 Hz). MS (*m*/*z*, Ru^{102}) 749.2 (M^+), 565.1 ($M^+ - N_3 - 2CCO_2CH_3$). Anal. Calcd for $C_{37}H_{35}N_3P_2O_4Ru$: C, 59.36; H, 4.71; N, 5.61. Found: C, 60.15; H, 4.92; N, 5.52.

Synthesis of *N*(2)-Bound Cp(dppe)Ru$N_3C_2HCO_2Me$ (3). To a Schlenk flask charged with **1** (202.1 mg, 0.334 mmol) were added methyl propiolate (140.1 mg, 148.2 μL, 1.668 mmol) and CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 8 h then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of *n*-pentane, giving a yellow precipitate. After filtration, the precipitate was washed with 2 × 10 mL of *n*-pentane and dried under vacuum to give the *N*(2)-bound Cp(dppe)Ru$N_3C_2HCO_2Me$ (**3**) (167.8 mg, 0.243 mmol, 73% yield). Spectroscopic data for **3** are as follows: IR (KBr, cm^{-1}) ν(CO) 1725 (vs), ν(N=N) 1438 (s), ν(C−O) 1227 (m). ^1H NMR ($CDCl_3$) δ 7.44−7.08 (m, 20H, Ph), 7.03 (s, 1H, CH), 4.58 (Cp), 3.65 (s, 3H, CH_3), 3.25−3.05, 2.70−2.50 (2m, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 88.20. ^{13}C NMR ($CDCl_3$) δ 162.4 (CO_2), 137.7 ($C(CO_2CH_3)$), 136.2 (CH), 133.0−127.5 (Ph), 82.1 (Cp), 50.7 (OCH_3), 28.9 (t, PCH_2CH_2P, J_{C-P} = 22.4 Hz). MS (*m*/*z*, Ru^{102}) 691.2 (M^+), 565.1 ($M^+ - N_3 - CH{\equiv}CCO_2CH_3$). Anal. Calcd for $C_{35}H_{33}N_3O_2P_2Ru$: C, 60.87; H, 4.82; N, 6.08. Found: C, 61.54; H, 4.89; N, 5.96.

Synthesis of *N*(2)-Bound Cp(dppe)RuN_3C_2HCN (4). To a Schlenk flask charged with **1** (220.5 mg, 0.364 mmol) were added fumaronitrile (125.5 mg, 1.603 mmol) and CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 12 h then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of *n*-pentane, giving a yellow precipitate. The precipitate was filtered, washed with 2 × 10 mL of *n*-pentane, and dried under vacuum to give the *N*(2)-bound Cp(dppe)RuN_3C_2HCN (**4**) (198.8 mg, 0.291 mmol, 80%yield). Spectroscopic data for **4** are as follows: IR (KBr, cm^{-1}) ν(C≡N) 2221 (vs), ν(N=N) 1432 (s). ^1H NMR ($CDCl_3$) δ 7.40−7.14 (m, 20H, Ph), 7.03 (s, 1H, CH), 4.58 (Cp), 3.20−3.00, 2.70−2.50 (2m, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 88.15. ^{13}C NMR (CDCl3) δ 137.6 (*C*(CN)), 136.2 (CH), 132.8−127.7 (Ph), 113.9 (CN), 82.2 (Cp), 28.8 (t, PCH_2CH_2P, J_{C-P} = 22.3 Hz). MS (*m*/*z*, Ru^{102}) 658.2 (M^+), 565.1 ($M^+ - N_3 - HCN$). Anal. Calcd for $C_{34}H_{30}N_4P_2Ru$: C, 62.10; H, 4.60; N, 8.52. Found: C, 62.68; H, 4.73; N, 8.46.

Synthesis of *N*(2)-Bound Cp(dppe)RuN_4C[C(CN)C(CN)$_2$] (5). To a Schlenk flask charged with **1** (200.5 mg, 0.331 mmol) and TCNE (200.9 mg, 1.570 mmol) was added CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 24 h then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of *n*-hexane. After filtration, the deep-blue precipitate was washed with 2 × 10 mL of *n*-hexane and dried under vacuum to give the *N*(2)-bound Cp(dppe)RuN_4C[C(CN)C(CN)$_2$] (**5**) (193.6 mg, 0.264 mmol, 80% yield). Spectroscopic data for **5** are as follows: IR (KBr, cm^{-1}) ν(C≡N) 2228 (s), 2196 (m), ν(N=N) 1432 (vs). ^1H NMR ($CDCl_3$) δ 7.59−7.13 (m, 20H, Ph), 4.76 (Cp), 3.30−3.10, 2.70−2.50 (2m,

(49) Bressan, M.; Rigo, P. *Inorg. Chem*. **1975**, *14*, 2286.

4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 86.97. ^{13}C NMR ($CDCl_3$) δ 154.9 ($C(CN)_2$), 140.8 (C(CN)), 133.1−128.1 (Ph), 126.1 (C=N), 112.0, 111.8, 110.9 (CN), 82.9 (Cp), 28.5 (t, PCH_2, J_{C-P} = 21.9 Hz). MS (m/z, Ru^{102}) 735.1 (M^+), 565.1 ($M^+ - N_3 - C_2(CN)_4$). Anal. Calcd for $C_{37}H_{29}N_7P_2Ru$: C, 60.49; H, 3.98; N, 13.35. Found: C, 61.63; H, 3.79; N, 13.47.

Synthesis of $N_3(CH_2C_6F_5)C_2(CO_2Me)_2$ (6a) and Other Organic Triazoles. To a Schlenk flask charged with **2** (200.1 mg, 0.268 mmol) and $BrCH_2C_6F_5$ (140 mg, 1.34 mmol) was added CH_2Cl_2 (20 mL). The resulting solution was stirred at about 40 °C for 48 h then the solvent was dried under vacuum. To the residue was added 10 mL of cold n-pentane. After filtration, the orange precipitate was washed with 2 × 10 mL of n-pentane and dried under vacuum to give the product Cp(dppe)RuBr (169.3 mg, 0.263 mmol, 98% yield). The filtrate was dried and extracted with 2 × 10 mL of cold n-pentane. The extract was filtered and the filtrate was dried under vacuum to give a mixture of the organic triazole $N_3(CH_2C_6F_5)C_2(CO_2Me)_2$ (**6a**) and the excess $BrCH_2C_6F_5$. Spectroscopic data for Cp(dppe)RuBr are as follows: ^1H NMR ($CDCl_3$) δ 7.85−7.09 (m, 20H, Ph), 4.56 (Cp), 2.80−2.60, 2.50−2.30 (2m, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 79.86. ^{13}C NMR ($CDCl_3$) δ 133.9−127.8 (Ph), 79.8 (Cp), 27.1 (t, PCH_2, J_{C-P} = 13.6 Hz). MS (m/z, Ru,^{102} Br^{81}) 646.1 (M^+), 565.2 (M^+ − Br). Anal. Calcd for $C_{31}H_{29}P_2RuBr$: C, 57.77; H, 4.54. Found: C, 58.02; H, 4.64. Spectroscopic data for **6a** are as follows: ^1H NMR ($CDCl_3$) δ 5.86 (s, 2H, CH_2), 3.98, 3.88 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 160.1, 158.6 (CO_2), 140.1, 132.0 ($C(CO_2CH_3)$), 146.0−136.4 (Ph), 53.6, 52.8 (OCH_3), 41.3 (CH_2). MS (m/z) 366.1 (M^++ 1). Complexes $N_3(CH_2Ph)C_2(CO_2Me)_2$ (**6b**) and $N_3(CH_2CO_2Me)C_2(CO_2Me)_2$ (**8c**) were prepared with similar procedure as that of **6a**. Spectroscopic data for **6b** are as follows: ^1H NMR ($CDCl_3$) δ 7.84−7.11 (m, 5H, Ph), 5.80 (s, 2H, CH_2), 3.98, 3.88 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 160.3, 158.7 (CO_2), 140.1, 133.8 ($C(CO_2CH_3)$), 137.9−127.8 (Ph), 53.8, 52.6 (OCH_3), 53.2 (CH_2). MS (m/z) 276.1 (M^+ + 1). Spectroscopic data for **6c** are as follows: ^1H NMR ($CDCl_3$) δ 5.42 (s, 2H, CH_2), 3.94, 3.92, 3.87 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 168.6, 164.4, 156.0 (CO_2), 143.8, 132.1 ($C(CO_2CH_3)$), 53.3, 52.7, 52.3 (OCH_3), 51.3 (CH_2). MS (m/z) 258.1 (M^+ + 1).

Synthesis of N(1)-Bound Cp(dppe)RuN$_3$(CH=CHCO$_2$Me)CHC(CO$_2$) (7). To a Schlenk flask charged with **1** (500.2 mg, 0.825 mmol) were added methyl propiolate (732 μL, 8.255 mmol) and $CHCl_3$ (25 mL). The mixture was stirred at room temperature for 5 days then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of n-pentane, giving a yellow precipitate. After filtration, the precipitate was washed with 2 × 10 mL of n-pentane and dried under vacuum to give a mixture of N(1)-bound (Z)- and (E)-Cp(dppe)RuN$_3$(CH=CHCO$_2$Me)CHC(CO$_2$) (**7**) (533.7 mg, 0.701 mmol, 85% yield, (Z)-**7**:(E)-**7** = 4:1). Spectroscopic data for (Z)-**7** are as follows: IR (KBr, cm^{-1}) ν(C=O) 1731 (vs), ν(COO$^-$) 1636 (vs), ν(N=N) 1432 (vs), ν(C−O) 1228 (m). ^1H NMR ($CDCl_3$) δ 7.59−7.13 (m, 21H, Ph and CH), 7.57 (d, 1H, J_{H-H} = 10.31 Hz, CH=CHCO$_2$), 5.42 (d, 1H, J_{H-H} = 10.31 Hz, CH=CHCO$_2$), 4.59 (Cp), 3.46 (s, 3H, CH_3), 2.91, 2.62 (m, 2H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 86.16. ^{13}C NMR ($CDCl_3$) δ 163.8, 158.2 (CO_2), 143.4 (CH), 140.6−128.5 (Ph, CCO$_2$, CH=CHCO$_2$), 112.1 (CH=CHCO$_2$), 82.4 (Cp), 51.4 (OCH_3), 28.7 (t, PCH_2CH_2P, J_{C-P} = 22.5 Hz). MS (m/z, Ru^{102}) 762.2 (M^+ + 1), 565.1 (M^+ − triazolato ring). Anal. Calcd for $C_{38}H_{35}N_3O_4P_2Ru$: C, 60.00; H, 4.64; N, 5.52. Found: C, 59.17; H, 4.87; N, 5.23. Spectroscopic data for (E)-**7** are as follows: ^1H NMR ($CDCl_3$) δ 8.65 (d, 1H, J_{H-H} = 14.32 Hz, CH=CHCO$_2$), 7.87 (s, 1H, CH), 7.59−7.13 (m, 20H, Ph), 4.95 (d, 1H, J_{H-H} = 14.32 Hz, CH=CHCO$_2$), 4.62 (Cp), 3.64 (s, 3H, CH_3), 2.91, 2.62 (m, 2H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 85.76. ^{13}C NMR ($CDCl_3$) δ 165.4, 157.9 (CO_2), 144.6 (CH), 139.7−128.2 (Ph, CCO$_2$, CH=CHCO$_2$), 110.6 (CH=CHCO$_2$), 82.2 (Cp), 51.7 (OCH_3), 27.7 (t, PCH_2CH_2P, J_{C-P} = 23.4 Hz). MS (m/z, Ru^{102}) 762.1 (M^+ + 1), 565.1 (M^+ − triazolato ring).

Synthesis of N(1)-Bound (Z)-{Cp(dppe)Ru-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$Me)}[I] (8a) and (Z)-{Cp(dppe)Ru-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$C$_6$F$_5$)}[Br] (8b). To a Schlenk flask charged with (Z)-**7** (85.1 mg, 0.112 mmol) and ICH_3 (35 μL, 0.560 mmol) was added CH_2Cl_2 (20 mL). The resulting solution was stirred at room temperature for 24 h, then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of diethyl ether. The yellow precipitate thus formed was filtered, washed with 2 × 10 mL of diethyl ether, and dried under vacuum to give the N(1)-bound (Z)-{Cp(dppe)-RuN$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$Me)}[I] (**8a**) (90.9 mg, 0.101 mmol) in 90% yield. Spectroscopic data for **8a** are as follows: IR (KBr, cm^{-1}) ν(C=O) 1731 (vs), 1720 (vs), ν(N=N) 1438 (vs), ν(C−O) 1228 (m). ^1H NMR ($CDCl_3$) δ 7.67 (s, 1H, CH), 7.50−7.21 (m, 20H, Ph), 6.68 (d, 1H, J_{H-H} = 9.23 Hz, CH=CHCO$_2$), 5.84 (d, 1H, J_{H-H} = 9.23 Hz, CH=CHCO$_2$), 4.74 (Cp), 3.94, 3.57 (s, 3H, OCH_3), 2.95, 2.66 (m, 2H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 84.45. ^{13}C NMR ($CDCl_3$) δ 162.4, 156.3 (CO_2), 144.3 (CH), 139.1−128.6 (Ph, CCO$_2$, CH=CHCO$_2$), 119.3 (CH=CHCO$_2$), 82.2 (Cp), 53.2, 52.0 (OCH_3), 29.0 (t, PCH_2CH_2P, J_{C-P} = 22.5 Hz). MS (m/z, Ru^{102}) 776.2 (M^+ − I), 565.1 (M^+ − triazolato ring). Anal. Calcd for $C_{39}H_{38}N_3P_2O_4RuI$: C, 51.89; H, 4.24; N, 4.66. Found: C, 51.11; H, 4.46; N, 4.38. Complex (Z)-{Cp(dppe)-Ru-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$C$_6$F$_5$)}[Br] (**8b**) (91.7 mg, 0.090 mmol, 85% yield from 80.3 mg of (Z)-**7**) was prepared by using a similar procedure as that of **8a**. Spectroscopic data for **8b** are as follows: ^1H NMR ($CDCl_3$) δ 7.50 (s, 1H, CH), 7.71−7.19 (m, 20H, Ph), 6.45 (d, 1H, J_{H-H} = 9.42 Hz, CH=CHCO$_2$), 5.76 (d, 1H, J_{H-H} = 9.42 Hz, CH=CHCO$_2$), 5.29 (s, 2H, CH_2), 4.70 (Cp), 3.54 (s, 3H, OCH_3), 2.86, 2.60 (m, 2H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 84.00. ^{13}C NMR ($CDCl_3$) δ 162.3, 155.3 (CO_2), 144.0 (CH), 139.0−128.0 (Ph, CCO$_2$, CH=CHCO$_2$), 119.4 (CH=CHCO$_2$), 82.1 (Cp), 54.8 (CH_2), 52.3 (OCH_3), 28.6 (t, PCH_2CH_2P, J_{C-P} = 22.6 Hz). MS (m/z, Ru^{102}) 942.2 (M^+ − Br), 565.1 (M^+ − triazolato ring). Anal. Calcd for $C_{45}H_{37}N_3P_2O_4RuF_5Br$: C, 52.90; H, 3.65; N, 4.11. Found: C, 51.78; H, 3.83; N, 3.97.

Synthesis of (Z)-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$Me) (9a) and (Z)-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$C$_6$F$_5$) (9b). To a Schlenk flask charged with (Z)-**7** (200.1 mg, 0.263 mmol) were added CH_2Cl_2 (20 mL) and ICH_3 (164 μL, 2.635 mmol). The resulting solution was stirred for 4 days at room temperature, then the solvent and ICH_3 were dried under vacuum. The residue was extracted with 2 × 10 mL of cold n-pentane. The extract was filtered and the filtrate was dried under vacuum to give a colorless liquid, (Z)-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$Me) (**9a**) (19.4 mg, 0.092 mmol, 35% yield). Spectroscopic data for **9a** are as follows: ^1H NMR ($CDCl_3$) δ 8.14 (s, 1H, CH), 7.62 (d, 1H, J_{H-H} = 9.29 Hz, CH=CHCO$_2$), 6.14 (d, 1H, J_{H-H} = 9.29 Hz, CH=CHCO$_2$), 3.92, 3.70 (OCH_3). ^{13}C NMR ($CDCl_3$) δ 165.5, 152.3 (CO_2), 137.3 (CH), 129.4 (CCO$_2$), 118.3 (CH=CHCO$_2$), 106.2 (CH=CHCO$_2$), 52.8, 52.2 (OCH_3). High-resolution MS (m/z): calcd for $C_8H_9N_3O_4$ 211.0591, found 211.0593. Complex (Z)-N$_3$(CH=CHCO$_2$Me)C$_2$H(CO$_2$C$_6$F$_5$) (**9b**) was prepared from (Z)-**7** with a 10-fold excess of $BrCH_2C_6F_5$ with use of a similar procedure as that of **9a**. The final product is still mixed with excess $BrCH_2C_6F_5$. Spectroscopic data for **9b** are as follows: ^1H NMR ($CDCl_3$) δ 8.16 (s, 1H, CH), 7.58 (d, 1H, J_{H-H} = 9.46 Hz, CH=CHCO$_2$), 6.15 (d, 1H, J_{H-H} = 9.46 Hz, CH=CHCO$_2$), 5.48 (OCH_2), 3.84 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 165.3, 157.3 (CO_2), 146.0, 142.7, 138.6, 136.6 (m, C_6F_5), 137.5 (CH), 129.4 (CCO$_2$), 118.8 (CH=CHCO$_2$), 114.5 (CH=CHCO$_2$), 52.3 (OCH_2), 52.2 (OCH_3).

Synthesis of N(1)-Bound {Cp(dppe)RuN$_3$(CH$_2$C$_6$F$_5$)-C$_2$HCO$_2$Me}[Br] (10a) and Other Triazolato Complexes. To a Schlenk flask charged with **3** (100.1 mg, 0.145 mmol) and $BrCH_2C_6F_5$ (109.4 μL, 0.724 mmol) was added CH_2Cl_2 (20 mL). The resulting solution was stirred at room temperature for 24 h, then the solvent was reduced to 2 mL under vacuum. To the residue was added 20 mL of n-pentane. The yellow precipitate thus formed was filtered, washed with 2 × 10 mL of n-pentane, and dried under vacuum to give the N(1)-bound

Table 5. Crystal and Intensity Collection Data for Complexes 2, 3, 4, 5, (*Z*)-7 and 10A

	2	**3**	**4**·CH_3CN[b]	**5**	(*Z*)-**7**·$CHCl_3$·$4H_2O$[b]	**10a**·CH_2Cl_2[b]
formula	$C_{37}H_{35}N_3O_4P_2Ru$	$C_{35}H_{33}N_3O_2P_2Ru$	$C_{36}H_{33}N_5P_2Ru$	$C_{37}H_{29}N_7P_2Ru$	$C_{39}H_{44}Cl_3N_3O_8P_2Ru$	$C_{43}H_{37}BCl_2N_3O_2P_2Ru$
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
a, Å	9.7530(1)	11.1619(5)	9.7544(18)	11.2596(4)	10.7371(2)	13.0361(1)
b, Å	15.9255(2)	17.1287(7)	11.985(3)	21.9688(8)	13.3434(3)	19.0355(2)
c, Å	21.2476(2)	16.2733(7)	14.798(3)	13.9563(5)	14.6027(3)	17.8451(2)
α, deg	90	90	92.01(2)	90	83.0903(9)	90
β, deg	93.790(1)	95.375(1)	93.22(2)	104.126(1)	80.0720(10)	100.1508(4)
γ, deg	90	90	111.584(19)	90	81.2726(10)	90
V, $Å^3$	3292.99(6)	3097.6(2)	1603.2(6)	3347.8(2)	2027.39(7)	4358.92(7)
Z	4	4	2	4	2	4
temp, K	150(1)	150(1)	295(2)	150(1)	150(1)	150(1)
diffractometer	CCD	CCD	CAD-4	CCD	CCD	CCD
d(calcd), Mg/m^3	1.510	1.481	1.447	1.458	1.560	1.590
abs coeff, mm^{-1}	0.619	0.647	0.623	0.602	0.719	0.636
F(000)	1536	1416	716	1496	976	2104
no. of reflns collected	22060	26329	7369	35027	35498	41178
no. of indep reflns	7444 (*R*(int) = 0.0320)	7120 (*R*(int) = 0.0618)	7369 (*R*(int) = 0.0000)	7694 (*R*(int) = 0.0358)	9295 (*R*(int) = 0.0637)	9893 (*R*(int) = 0.0472)
GOF[a] on F^2	1.088	1.014	1.056	1.050	1.029	1.079
R ($I > 2\sigma(I)$)	R1 = 0.0414, wR2 = 0.0910	R1 = 0.0362, wR2 = 0.0585	R1 = 0.0293, wR2 = 0.0787	R1 = 0.0290, wR2 = 0.0707	R1 = 0.0584, wR2 = 0.1481	R1 = 0.0460, wR2 = 0.1136
R (all data)	R1 = 0.0574, wR2 = 0.0979	R1 = 0.0732, wR2 = 0.0694	R1 = 0.0344, wR2 = 0.0814	R1 = 0.0410, wR2 = 0.0734	R1 = 0.0940, wR2 = 0.1727	R1 = 0.0712, wR2 = 0.1309
peak, hole, e $Å^{-3}$	0.991, −1.214	0.522, −0.427	0.587, −0.802	1.500, −0.492	1.030, −1.139	1.009, −0.825

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* and *p* denote the number of data and the number of parameters. R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 1.2129P]$ and $P = (F_o^2 + 2F_c^2)/3$. [b] The solvent was found to incorporate with the crystals.

{Cp(dppe)RuN_3($CH_2C_6F_5$)C_2HCO_2Me}[Br] (**10a**) (126.9 mg, 0.133 mmol) in 92% yield. Spectroscopic data for **10a** are as follows: IR (KBr, cm^{-1}) ν(C=O) 1738 (vs), ν(N=N) 1438 (vs), ν(C−O) 1222 (m). ^{1}H NMR ($CDCl_3$) δ 8.43 (s, 1H, CH), 7.67−7.06 (m, 20H, Ph), 4.97 (s, 2H, CH_2), 4.62 (Cp), 3.96 (s, 3H, OCH_3), 2.74, 2.71 (2 br, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 86.23. ^{13}C NMR ($CDCl_3$) δ 157.0 (CO_2), 146.0 (CH), 140.1−128.3 (Ph and *C*(CO_2)), 82.6 (Cp), 53.4 (OCH_3), 39.4 (CH_2), 28.9 (t, PCH_2CH_2P, J_{C-P} = 22.3 Hz). MS (*m*/*z*, Ru^{102}) 872.0 (M^+ − Br), 565.0 (M^+ − Br − $CH_2C_6F_5$ − N_3 − $C_2HCO_2CH_3$). Anal. Calcd for $C_{42}H_{35}N_3P_2O_2RuF_5Br$: C, 53.01; H, 3.71; N, 4.42. Found: C, 54.11; H, 3.80; N, 4.39. Complex {Cp(dppe)RuN_3(CH_2Ph)C_2HCO_2Me}[Br] (**10b**) (108.7 mg, 0.126 mmol, 87% yield from 100.2 mg of **3**), {Cp(dppe)RuN_3(CH_2CO_2Me)C_2HCO_2Me}[Br] (**10c**) (109.9 mg, 0.130 mmol, 90% yield from 100.0 mg of **3**), and {Cp(dppe)RuN_3(CH_3)C_2HCO_2Me}[I] (**10d**) (102.4 mg, 0.123 mmol, 83% yield from 102.3 mg of **3**) were prepared by using a similar procedure as that of **10a**. Spectroscopic data for **10b** are as follows: ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1H, CH), 7.41−7.09 (m, 25H, Ph), 4.85 (s, 2H, CH_2), 4.70 (Cp), 3.83 (s, 3H, CH_3), 2.76−2.64 (m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$) δ 85.84. ^{13}C NMR ($CDCl_3$) δ 156.6 (CO_2), 146.2 (CH), 139.6−126.7 (Ph and *C*(CO_2)), 82.1 (Cp), 53.6 (CH_2), 53.1 (OCH_3), 28.7 (t, PCH_2, J_{C-P} = 23.8 Hz). MS (*m*/*z*, Ru^{102}) 782.1 (M^+ − Br), 565.0 (M^+ − Br − CH_2Ph − N_3 − $C_2HCO_2CH_3$). Anal. Calcd for $C_{42}H_{40}N_3P_2O_2RuBr$: C, 58.54; H, 4.68; N, 4.88. Found: C, 59.13; H, 4.77; N, 4.78. Spectroscopic data for **10c** are as follows: ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H, CH), 7.80−7.06 (m, 25H, Ph), 4.70 (Cp), 4.44 (s, 2H, CH_2), 3.85, 3.51 (s, 3H, CH_3), 3.00−2.60 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 84.43. ^{13}C NMR ($CDCl_3$) δ 164.5, 156.6 (CO_2), 145.1 (CH), 139.0−127.6 (Ph and *C*(CO_2)), 81.9 (Cp), 53.2, 52.9 (OCH_3), 50.6 (CH_2), 28.4 (t, PCH_2, J_{C-P} = 21.0 Hz). MS (*m*/*z*, Ru^{102}) 764.1 (M^+ − Br), 565.0 (M^+ − Br − $CH_2CO_2CH_3$ − N_3 − $C_2HCO_2CH_3$). Anal. Calcd for $C_{38}H_{38}N_3P_2O_2RuBr$: C, 54.10; H, 4.54; N, 4.98. Found: C, 53.87; H, 4.63; N, 4.85. Spectroscopic data for **10d** are as follows: ^{1}H NMR ($CDCl_3$) δ 8.18 (s, 1H, CH), 7.83−7.06 (m, 25H, Ph), 4.76 (Cp), 3.88 (s, 3H, CH_3), 3.26 (s, 3H, NCH_3), 2.97, 2.67 (m, 2H, PCH_2). ^{31}P NMR ($CDCl_3$) δ 84.90. ^{13}C NMR ($CDCl_3$) δ 156.8 (CO_2), 145.8 (CH), 134.1−127.7 (Ph and *C*CO_2), 82.1 (Cp), 53.2 (OCH_3), 37.4 (NCH_3), 29.0 (t, PCH_2, J_{C-P} = 22.6 Hz). MS (*m*/*z*, Ru^{102}) 706.1 (M^+ − I), 565.0 (M^+ − I − CH_3 − N_3 − $C_2HCO_2CH_3$). Anal. Calcd for $C_{36}H_{36}N_3P_2O_2RuI$: C, 51.93; H, 4.36; N, 5.05. Found: C, 51.63; H, 4.54; N, 4.92.

X-ray Analysis. Single crystals suitable for X-ray diffraction study were grown as mentioned above. The chosen single crystal was glued to a glass fiber and mounted on a SMART CCD or a CAD4 diffractometer. The data were collected with use of 3-kW sealed-tube molybdenum Kα radiation (λ = 0.7107 Å). Intensity was intergrated and absorption corrections were applied by using SADABS.[50] Data were processed and refined by using the SHELXTL[51] program. Hydrogen atoms were placed geometrically, using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. Crystal data for **2**, **3**, **4**, **5**, (*Z*)-**7**, and **10a** are listed in Table 5. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

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Supporting Information Available: Details about the X-ray crystal structures, including diagrams, and the tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2**, **3**, **4**, **5,** (*Z*)-**7** and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(51) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.