J. Am. Chem. Soc. 1989, 111, 3258-3271

coplanarities minimize, in the absence of angular distortion, the distances between C7 and O (3.004 (4) Å) and C11 and F (2.860 (5) Å). In this case, the hydrogen atoms on C7 and C17 appear to be staggered with respect to O and F, respectively (H71-O = 2.685 Å, H73-O = 2.697 Å); H171-F = 2.486 Å, H173-F = 2.624 Å).

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE85-04737) is gratefully acknowledged. We also thank the NSF and the San Diego Supercomputer Center for a generous allocation of computer time.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables SI-III for **1**, Tables IV-VI for **2**, and Tables VII-IX for **3**) (16 pages); tables of calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

Synthesis of Alkylruthenium Nitrosyl Complexes. Migratory Insertion to Coordinated Nitric Oxide and the Mechanism of the Conversion of the Resultant Nitrosoalkyl Compounds to Oximate, Carboxamide, and Cyano Compounds

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Abstract: The compounds $(\eta^5\text{-}C_5Me_5)Ru(NO)R_2$ (**2a**, R = CH_3; **2b**, R = CH_2CH_3) were synthesized by treating $(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2$ (**1**) with alkylating agents. Thermolysis of **2a** with PMe_3 gave $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CN$ (**3**), H_2O, and CH_4; heating **2b** with PMe_3 produced $(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PMe_3)_2$ (**4**) and ethane. The reaction of **1** with PhMgCl followed by protonolysis with HCl gave $(\eta^5\text{-}C_5Me_5)Ru(NO)(Ph)(Cl)$ (**5**); treatment of **5** with EtMgCl gave $(\eta^5\text{-}C_5Me_5)Ru(NO)(Ph)(Et)$ (**6**). Thermolysis of **6** with PMe_3 gave **4**; however, thermolysis of **6** with $PPhMe_2$ led to the NO insertion product $(\eta^5\text{-}C_5Me_5)Ru(N(O)CH_2CH_3)(Ph)(PPhMe_2)$ (**8**), characterized by X-ray diffraction (crystal data: space group $P2_1/c$; $a = 8.6946$ (6) Å, $b = 10.749$ (1) Å, $c = 26.946$ (3) Å, $\beta = 95.7$ (4)°; $V = 2505.9$ (8) Å^3; 3263 unique data, 2795 for which $F^2 > 3\sigma(F^2)$; $R = 2.20\%$, $wR = 2.98\%$, GOF = 1.88). Heating complex **8** with PMe_3 produced **4** while heating for extended periods with $PPhMe_2$ gave $(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PPhMe_2)_2$ (**9**). The conversion of **8** to **9** was found to proceed under milder conditions in the presence of a strong Brønsted base catalyst (e.g., $NaOSiMe_3$); using $CNBu^t$ in place of $PPhMe_2$ afforded $(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PPhMe_2)(CNBu^t)$ (**11**). Treatment of **8** with the stronger base $KN(SiMe_3)_2$ in the presence of $PPhMe_2$ led to $(\eta^5\text{-}C_5Me_5)Ru(Ph)(PPhMe_2)_2$ (**12**) and $KONCHCH_3$. Reaction of **8** with $KN(SiMe_3)_2$ and 18-crown-6 gave $[(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(Ph)(PPhMe_2)]^-[K^+\cdot crown]$ (**13**). Complex **13** reacts with $PPhMe_2$ to give **12** and with Et_3SiOH and $PPhMe_2$ to generate **9**. Mechanistic studies, including kinetics, isotope effect, and tracer experiments, indicate that conversion of **8** to **4**, **9**, and **12** is initiated by the base abstraction of a methylene proton of the nitrosoethane ligand. Upon further thermolysis, **4** rearranges to $(\eta^5\text{-}C_5Me_5)Ru(N(H)C(O)CH_3)(PMe_3)_2$ (**14**). A possible mechanism for this transformation is discussed.

The discovery and elucidation of metal-mediated processes that form new bonds in organic compounds are important goals in organometallic chemistry. Partly in response to this, a significant amount of research has focused on the synthesis and reactivity of organotransition-metal nitrosyl compounds; among the desired properties of these complexes would be their reactions to form new carbon-nitrogen bonds.[1]

Considerable progress has been made in this area. Among the better understood C-N bond-forming reactions is migratory insertion of nitric oxide into metal-carbon bonds;[2] mechanistic studies[3] have established the close similarity of this reaction to the better known metal-carbonyl insertion reaction.[4] The unusual reaction between $(\eta^5\text{-}C_5H_5)Co(NO)_2$ and alkenes has also been thoroughly investigated.[5]

Studies of nitrosyl-transition metal compounds have proven useful in modeling the heterogenous metal-catalyzed oxidation of propene by NO to form acrylonitrile.[6] A group at Dupont has discovered[7] that η^3-allylnickel bromide dimer reacts with nitric oxide to form $(\eta^2\text{-}CH_2{=}CHCH(NOH))Ni(NO)Br$. In subsequent years, closely related chemistry of allyl and nitrosyl ligands was uncovered for other transition metals.[8]

Earlier, we communicated our initial results concerning the chemistry of some new alkylnitrosylruthenium compounds, the thermolysis of which produced unusual ruthenium cyanide, η^1-oximate, and η^1-carboxamide complexes.[9] Migratory insertion

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[1] (a) Pandey, K. K. *Coord. Chem. Rev.* **1983**, *51*, 69-98. (b) Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317-355.

[2] See, for example: (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155-164. (b) Fochi, G.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C. *J. Chem. Soc., Dalton Trans.* **1986**, 445-447. (c) Jones, C. J.; McCleverty, J. A.; Rothin, A. S. *Ibid.* **1985**, 405-407. (d) Middleton, A. R.; Wilkinson, G. *Ibid.* **1981**, 1898-1905. (e) Middleton, A. R.; Wilkinson, G. *Ibid.* **1980**, 1888-1892. (f) Shortland, A. J.; Wilkinson, G. *Ibid.* **1973**, 872-876. (g) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 1453-1464. (h) Goldhaber, A.; Vollhardt, K. P. C.; Walborsky, E. C.; Wolfgruber, M. *J. Am. Chem. Soc.* **1986**, *108*, 516-518.

[3] (a) Weiner, W. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3922-3929. (b) Weiner, W. P.; White, M. A.; Bergman, R. G. *Ibid.* **1981**, *103*, 3612-3614. (c) Seidler, M. D.; Bergman, R. G. *Organometallics* **1983**, *2*, 1897-1899. (d) Diel, B. N. *J. Organomet. Chem.* **1985**, *284*, 257-262.

[4] (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195-225. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299-311.

[5] Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 2985-2995 and references therein.

[6] (a) England, D. C.; Mock, G. V. U.S. Patent 2736739, 1956. (b) England, D. C.; Foster, R. E. U.S. Patent 3023226, 1962. (c) Arai, H.; Iida, H.; Kunugi, T. *J. Catal.* **1970**, *17*, 396-398.

[7] (a) Clement, R. A. U.S. Patent 3652620, 1972. (b) Clement, R. A.; Klabunde, U.; Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 87-94.

[8] Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880-1882 and references therein.

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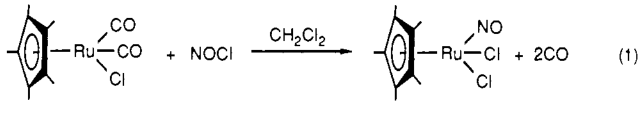
of the alkyl ligands to the bound NO group was proposed to be a key step in these thermal reactions. Herein we report the full experimental details of this chemistry, examples of new reactions in this system, and a detailed mechanistic study of this unique group of chemical transformations.

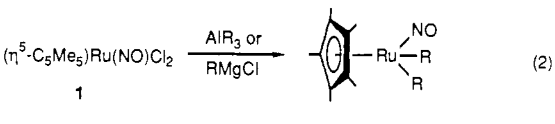
Results

Treatment of (η^5-C_5Me_5)Ru(CO)$_2$Cl[10] with NOCl in CH_2Cl_2 at ambient temperature led to the formation of (η^5-C_5Me_5)Ru(NO)Cl_2 (**1**) (eq 1),[11] isolated as dark green air-stable crystals in 50–60% yield. Compound **1** has an intense IR absorption at 1790 cm^{-1}, consistent with the presence of a linear terminally bound nitrosyl ligand.



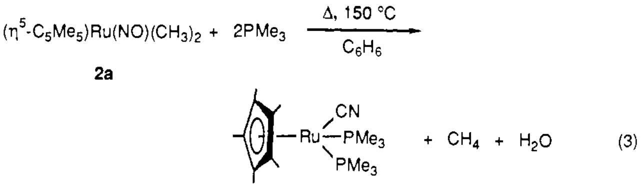
1

After experimenting with a variety of alkylating agents, the transformation of **1** to dialkyl complexes **2** was found to be most cleanly achieved with trialkylaluminum or Grignard reagents (eq 2). The dimethyl complex (η^5-C_5Me_5)Ru(NO)$(CH_3)_2$ (**2a**) was obtained in 67% yield and its diethyl analogue (η^5-C_5Me_5)Ru(NO)$(CH_2CH_3)_2$ (**2b**) in 56% yield following sublimation at 10^{-4} Torr. Complexes **2** were characterized by standard techniques (see Experimental Section). Both **2a** and **2b** are slightly air-sensitive low-melting crystalline solids that are extremely soluble in the usual organic solvents. Compounds **2a** and **2b** show intense IR absorptions at 1735 and 1720 cm^{-1}, respectively, consistent with the presence of linear terminally bound nitric oxide ligands.



2a, R = CH_3
2b, R = CH_2CH_3

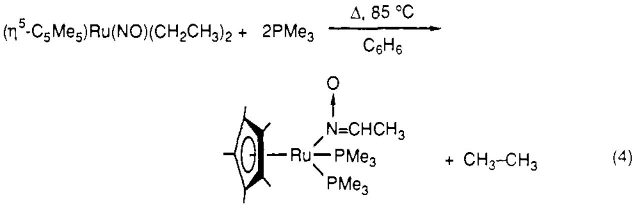
Thermolysis of Nitrosyldialkylruthenium Complexes. Complex **2a** decomposes slowly in benzene at 120 °C over 24 h, leading to intractable products. However, thermolysis in benzene at 150 °C for 20 h in the presence of trimethylphosphine (eq 3) produced a new material having an intense IR absorption at 2060 cm^{-1}.



3

Spectrometric and analytical data are consistent with the formulation of this material as the metal cyanide (η^5-C_5Me_5)Ru$(PMe_3)_2$CN (**3**).[12] Compound **3** was isolated as yellow crystals in 51% yield by recrystallization; it was prepared independently by treatment of (η^5-C_5Me_5)Ru$(PMe_3)_2$Cl[13] with KCN in methanol in 91% yield. The transformation of **2a** to **3** also produced 1 equiv of both water and methane as the only volatile products (determined by GC/MS, ^{1}H NMR spectrometry, and Toepler pump analysis; see Experimental Section).

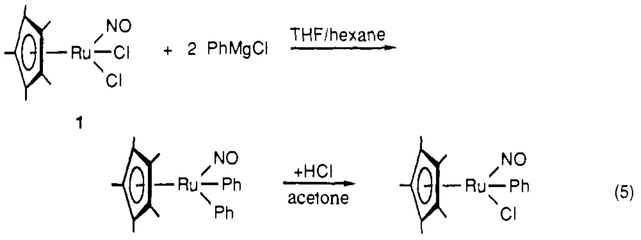
Insight as to how the cyanide complex **3** may be formed from **2a** was provided by thermolysis of diethyl complex **2b** in the presence of trimethylphosphine (eq 4). The reaction proceeded



4

at the somewhat lower temperature of 85 °C in benzene and gave a yellow solid in 76% yield, identified on the basis of spectral and analytical data as the N-bound ruthenium oximate **4** shown in eq 4.[14] That the carbon attached to the nitrogen is sp^2-hybridized is confirmed by the single-bond ^{13}C–^1H coupling constant of 172.7 Hz measured in the proton-coupled carbon spectrum. The chemical shift of this carbon at δ 140.53 ppm and the absence of any strong coupling to ^{31}P makes direct attachment of this atom to the ruthenium improbable. The volatile materials produced in this reaction were 0.82 equiv of ethane and 0.09 equiv of ethylene (as determined by GC/MS and quantified by GC and Toepler pump analysis).

Synthesis of (η^5-C_5Me_5)Ru(NO)(Ph)(Cl) (5) and (η^5-C_5Me_5)Ru(NO)(Ph)(CH_2CH_3) (6). The new complex (η^5-C_5Me_5)Ru(NO)(Ph)(Cl) (**5**) was prepared by protonolysis of (η^5-C_5Me_5)Ru(NO)Ph_2 with HCl (eq 5). Crude (η^5-C_5Me_5)Ru(NO)Ph_2 was prepared by treatment of (η^5-C_5Me_5)Ru(NO)Cl_2 (**1**) with 2 equiv of PhMgCl.[15] After removal of excess Grignard reagent by filtration through silica gel, concentration, and redissolution in acetone, the mixture was treated with slightly more than 1 equiv of aqueous HCl. Complex **5** was obtained analytically pure by column chromatography on silica gel in 65–75% yields as dark red-brown crystals. Addition of two or more equivalents of HCl to the diphenyl complex led to complete reversion to **1**.



5

Phenyl(chloro)ruthenium compound **5** is an air- and moisture-stable solid. Reaction of **5** with CH_3CH_2MgCl produced (η^5-C_5Me_5)Ru(NO)(Ph)(CH_2CH_3) (**6**) (eq 6), obtained as slightly air-sensitive dark red flakes in 60–70% yield.

5 **6**

Thermolysis of 6 with Phosphines. Heating a benzene solution of phenyl-ethyl complex **6** at 85 °C led to intractable products. In the presence of PMe_3 at 85 °C, however, the bisphosphine oximate complex **4** was formed as reported for the diethyl analogue **2b**. Monitoring the reaction by ^{1}H NMR spectrometry revealed the formation of an intermediate product, **7**, which was too sen-

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(9) Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6110–6111.

(10) Heinekey, D. M. Ph.D. Dissertation, University of Alberta, Edmonton, Alberta, 1981.

(11) (η^5-C_5Me_5)Ru(NO)Cl_2 (**1**) has been prepared independently: Efraty, A.; Elbaze, G. *J. Organomet. Chem.* **1984**, *260*, 331–334.

(12) (η^5-C_5Me_5)Ru$(PMe_3)_2$CN has been prepared independently: Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.

(13) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278.

(14) This is a reformulation of the structure we proposed earlier.[9] That the oximate ligand is bound to ruthenium through the nitrogen atom rather than the oxygen atom was determined by a preliminary X-ray diffraction study of the bis(phenyldimethylphosphine) analogue **9**. Details will be reported at a later date.

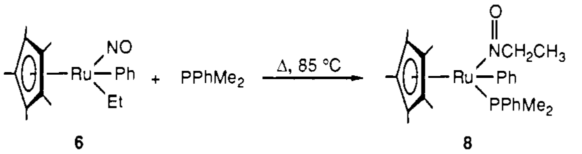
(15) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298–4304.

Table I. Selected Intramolecular Distances[a] and Esd's (Å) for Complex **8**

atom 1	atom 2	distance
Ru	P	2.292 (1)
Ru	N	1.918 (2)
Ru	C11	2.094 (2)
Ru	C1	2.284 (2)
Ru	C2	2.266 (2)
Ru	C3	2.255 (2)
Ru	C4	2.308 (2)
Ru	C5	2.305 (2)
Ru	CP	1.938
N	O	1.258 (2)
N	C25	1.495 (3)
C25	C26	1.463 (4)
C11	C12	1.390 (3)
C12	C13	1.395 (3)
C13	C14	1.371 (4)
C14	C15	1.376 (3)
C15	C16	1.390 (3)
C16	C11	1.399 (3)
C1	C2	1.413 (3)
C1	C5	1.417 (3)
C1	C6	1.511 (3)
C2	C3	1.435 (3)
C2	C7	1.501 (3)
C3	C4	1.413 (3)
C3	C8	1.501 (3)
C4	C5	1.420 (3)
C4	C9	1.507 (3)
C5	C10	1.510 (3)
P	C17	1.830 (2)
P	C23	1.836 (3)
P	C24	1.826 (2)
C17	C18	1.394 (3)
C18	C19	1.379 (4)
C19	C20	1.344 (4)
C20	C21	1.369 (5)
C21	C22	1.389 (4)
C22	C17	1.366 (3)

[a] Cp is the centroid of the pentamethylcyclopentadiene ring.

sitive to isolate (Scheme I). Although the entire spectrum of **7** could not be completely resolved, clearly evident were single PMe_3 and C_5Me_5 resonances (δ 0.99 (d, 9 H, J_{HP} = 9.4 Hz), 1.51 (d, 15 H, J_{HP} = 1.1 Hz) ppm), two multiplets integrating as single protons at δ 3.70 and 3.90 ppm, and resonances in the aryl region of the spectrum. On the basis of these signals, compound **7** was tentatively identified as the product formed from migratory insertion of the ethyl group to the NO ligand, $(\eta^5\text{-}C_5Me_5)Ru(N(O)CH_2CH_3)(Ph)(PMe_3)$. Fortunately, the thermolysis of **6** at 85 °C with $PPhMe_2$ instead of PMe_3 gave an analogous complex **8** which in this case was isolable as an intensely dark red nonvolatile solid, very soluble in common organic solvents (eq 7). This material was obtained in 65–75% yield as dark red crystals and analyzed correctly for $C_{26}H_{31}NOPRu$.



(7)

The structure of compound **8** was confirmed by a single-crystal X-ray diffraction study. Suitable crystals were obtained by slow crystallization from concentrated pentane solutions at −30 °C. An ORTEP diagram and labeling scheme for complex **8** is given in Figure 1. Interatomic bond distances and angles are listed in Tables I and II. The molecule appears in the expected pseudooctahedral, three-legged piano stool configuration. The ligand–ruthenium–ligand bond angles for the nitrosoethyl, phenyl, and phosphine moieties deviate less than 10° from the 90° expected for a pseudooctahedral configuration. The η^1-coordination of the nitrosoethyl group is confirmed; the nitrosoethane ligand is bound solely through the nitrogen with a Ru–N bond distance of 1.918 (2) Å.

Scheme I

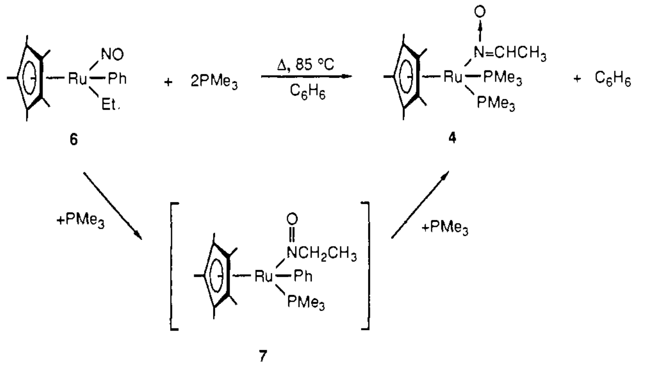


Table II. Intramolecular Bond Angles[a] (deg) and Esd's for Complex **8**

atom 1	atom 2	atom 3	angle
Cp	Ru	P	128.9
Cp	Ru	N	130.4
Cp	Ru	C11	119.6
P	Ru	N	88.56 (5)
P	Ru	C11	83.11 (6)
N	Ru	C11	92.60 (8)
Ru	N	O	128.86 (15)
Ru	N	C25	121.81 (14)
O	N	C25	109.26 (18)
N	C25	C26	112.44 (24)
Ru	C11	C12	122.16 (15)
Ru	C11	C16	122.19 (15)
C12	C11	C16	115.65 (19)
C11	C12	C13	122.10 (22)
C12	C13	C14	120.40 (23)
C13	C14	C15	119.42 (21)
C14	C15	C16	119.69 (23)
C11	C16	C15	122.71 (21)
C2	C1	C5	109.00 (19)
C1	C2	C3	106.95 (19)
C2	C3	C4	108.29 (18)
C3	C4	C5	108.05 (19)
C1	C5	C4	107.67 (19)
C2	C1	C6	126.28 (23)
C5	C1	C6	124.34 (23)
C1	C2	C7	126.04 (20)
C3	C2	C7	125.37 (20)
C2	C3	C8	126.20 (21)
C4	C3	C8	124.60 (20)
C3	C4	C9	124.49 (21)
C5	C4	C9	126.85 (22)
C1	C5	C10	124.82 (23)
C4	C5	C10	126.43 (23)
Ru	P	C17	115.95 (7)
Ru	P	C23	115.75 (8)
Ru	P	C24	119.23 (9)
C17	P	C23	100.60 (11)
C17	P	C24	102.18 (11)
C23	P	C24	100.24 (13)
P	C17	C18	121.17 (19)
P	C17	C22	121.38 (17)
C18	C17	C22	117.44 (21)
C17	C18	C19	121.3 (3)
C18	C19	C20	120.1 (3)
C19	C20	C21	120.1 (3)
C20	C21	C22	120.1 (3)
C21	C22	C17	120.90 (25)

[a] Cp is the centroid of the pentamethylcyclopentadiene ring.

The rate of thermolysis of phenyl–ethyl compound **6** in the presence of $PPhMe_2$ to generate nitrosoethyl compound **8** could

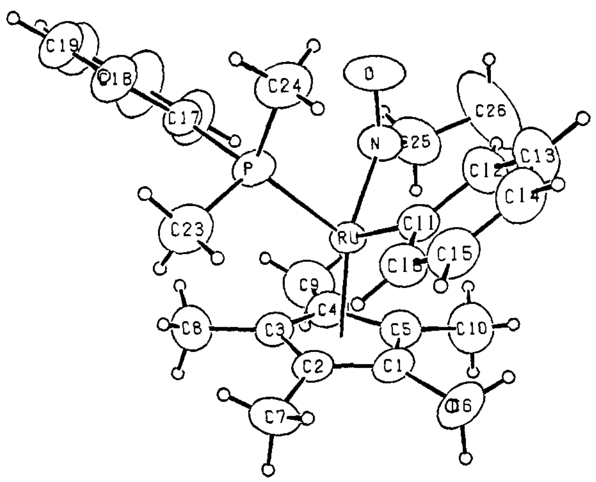


Figure 1. Geometry and labeling scheme for (η^5-C_5Me_5)Ru(N(O)-CH_2CH_3)(Ph)($PPhMe_2$) (**8**). The ellipsoids are scaled to represnt the 50% probability surface. Hydrogen atoms are given as arbitrarily small spheres for clarity.

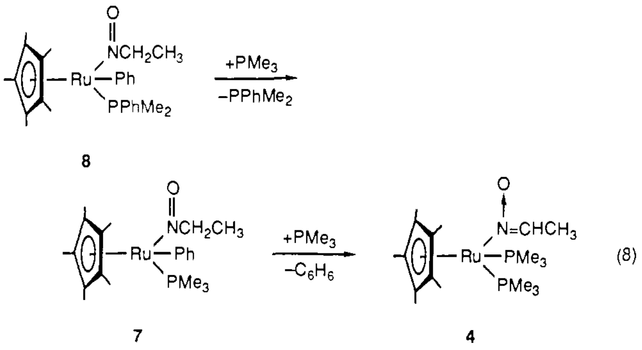
Table III. First-Order Rate Constants for (η^5-C_5Me_5)Ru(NO)(Ph)(Et) (**6**) + $PPhMe_2$ in C_6D_6 at 85 °C

10^2[**6**], M	[$PPhMe_2$]	k_{obs},[a] s^{-1}
2.21	0.100	2.8×10^{-4}
2.31	0.261	3.1×10^{-4}
2.16	0.445	2.9×10^{-4}
1.21	0.143	2.9×10^{-4}

[a] All values ±10%.

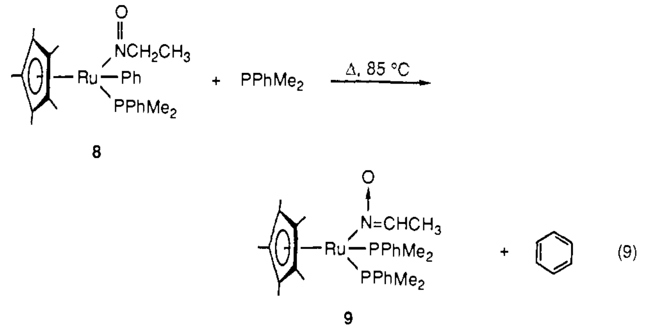
be conveniently followed by ^1H NMR spectrometry; rate data are given in Table III. The amount of **6** was quantified by integration of the C_5Me_5 resonance versus ferrocene internal standard. The reaction is cleanly first order in **6** with no observed dependence on $PPhMe_2$ concentration.

Reaction of 8 with Phosphines. Heating nitrosoethyl complex **8** with PMe_3 in benzene at 100 °C for 20 h leads primarily (ca. 70%) to oximate compound **4**, C_6H_6, and free $PPhMe_2$ (eq 8).



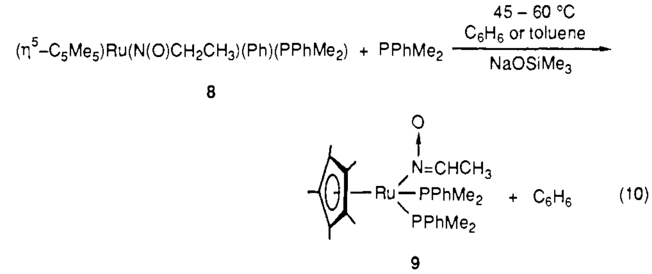
(8)

When the reaction is monitored by ^1H NMR spectrometry, it can be observed that **8** undergoes phosphine exchange to give complex **7** prior to conversion to the bisphosphine complex. This reaction testifies to the robust nature of the ruthenium-nitrogen bond in **8**; no substitution by phosphine is observed. The thermal reaction of **8** with $PPhMe_2$ is a much slower and less clean process; prolonged heating at 85 °C over many days eventually leads to the formation of (η^5-C_5Me_5)Ru((NO)$CHCH_3$)($PPhMe_2$)$_2$ (**9**) (vide infra) as the main organometallic product (68%) (eq 9).



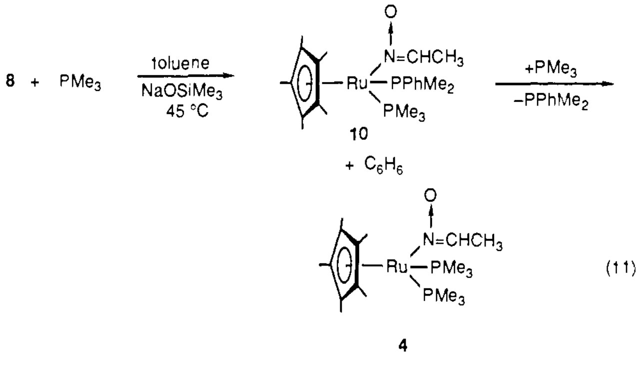
(9)

Reaction of 8 with Bases. Contrary to our expectations, in qualitative experiments we observed that the rate of conversion of **8** to **9** *increased* with greater concentrations of $PPhMe_2$. This strongly implies that free $PPhMe_2$ is somehow involved in the rate-determining step for conversion of **8** to **9**. It occurred to us that $PPhMe_2$ might be functioning as a proton-removing (Brønsted) base rather than a Lewis base in this reaction. To test this hypothesis, nitrosoethyl-ruthenium compound **8** was treated with a variety of stronger bases in the presence of phosphine. Significantly, the reaction of nitrosoethyl-ruthenium complex **8** with $NaOSiMe_3$ in the presence of $PPhMe_2$ in benzene or toluene occurs much more rapidly than when phosphine is present as the only base. In contrast to the reactions with phosphine, which occur at a reasonable rate at 85 °C, the $NaOSiMe_3$-induced reaction leads again to oximate product **9**, but goes rapidly at 45–60 °C (eq 10). Compound **9** is produced in 91% yield by ^1H NMR integration versus internal ferrocene standard; an 83% yield of bright lemon yellow crystals is isolated after crystallization from pentane at −30 °C. Oximate–bisphosphine complex **9** is very soluble in organic solvents and is air-sensitive both in solution and in the solid state. The formulation of **9** is clearly supported by spectrometric and analytical data (see Experimental Section). Analysis of the volatile materials from the formation of complex **9** by ^1H NMR spectrometry, GC, and GC/MS showed the production of 0.91 equiv of benzene. Importantly, $NaOSiMe_3$ can be recovered; the reaction can also be run with catalytic (0.1 equiv) amounts of $NaOSiMe_3$.



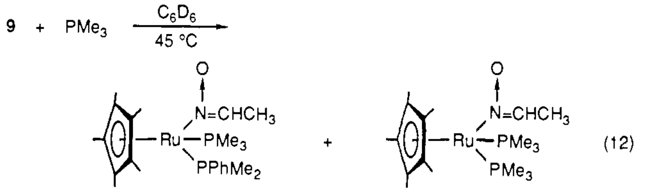
(10)

In order to determine whether the $PPhMe_2$ ligand leaves the coordination sphere of the ruthenium during the reaction, compound **8** was treated with $NaOSiMe_3$ in the presence of PMe_3 in C_6D_6 at 45 °C and the reaction monitored by ^1H NMR spectrometry (eq 11). The initially formed major product is the mixed bisphosphine–oximate complex (η^5-C_5Me_5)Ru((NO)$CHCH_3$)-($PPhMe_2$)(PMe_3) (**10**) along with some bis(trimethylphosphine) compound **4**. As the reaction proceeds, the major product becomes compound **4**. As a control, compound **9** was heated at 45 °C with an excess of PMe_3 and the solution was periodically monitored by ^1H NMR spectrometry (eq 12). Extensive phosphine exchange was observed over several hours to give the mixed phosphine complex **10** and the bis(trimethylphosphine) complex **4**; only trace amounts of **9** remained.



(11)

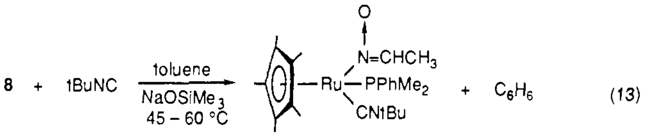
Compound **8** was also treated with $NaOSiMe_3$/18-crown-6 and $PPhMe_2$ in the course of our kinetic study (vide infra). The use



10 **4**

of a 1:1 equimolar $NaOSiMe_3$/18-crown-6 mixture greatly accelerated the reaction; clean, complete conversion of **8** to **9** occurred within several minutes at ambient temperature. Without $PPhMe_2$, the reaction produced intractable products.

The reaction of complex **8** with $NaOSiMe_3$ in the presence of *t*-BuNC in benzene or toluene gave $(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PPhMe_2)(CNBu^t)$ (**11**) and benzene (eq 13). The



11

reaction is quantitative by ^1H NMR spectrometry; crystallization from pentane at −30 °C afforded 75% of **11** as analytically pure pale yellow crystals. No bis-isocyanide product was observed, even when the reaction was carried out in the presence of a large excess of *t*-BuNC.

Treatment of a mixture of **8** and $PPhMe_2$ in toluene with $KN(SiMe_3)_2$ at ambient temperature produced a rapid color change from dark red to bright yellow along with the deposition of a white solid (Scheme II). A single new organometallic product was isolated by column chromatography in 86% yield as a yellow solid; the reaction is quantitative by ^1H NMR spectrometry. In the alkyl region of the ^1H NMR spectrum of the new compound, resonances are observed that indicate the ligation of two phosphine molecules to the ruthenium center (δ 1.25 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 7.5$ Hz), 1.46 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 7.1$ Hz), 1.54 (t, 15 H, $J_{HP} = 1.2$ Hz) ppm). NMR, mass, and elemental analysis data on this complex are consistent with its formulation as $(\eta^5\text{-}C_5Me_5)Ru(Ph)(PPhMe_2)_2$ (**12**). Phenyl compound **12** is nonvolatile, reasonably soluble in organic solvents, and air-stable in the solid state.

Analysis of the volatile components of the reaction mixture by ^1H NMR spectrometry and GC indicated the formation of 1 equiv of $HN(SiMe_3)_2$. The white precipitate from the reaction was identified as $KONCHCH_3$ by hydrolysis with H_2O followed by comparison with an authentic sample of $HONCHCH_3$ (acetaldehyde oxime) using ^1H NMR spectrometry and GC analysis. Reaction of compound **8** with CH_3CH_2MgCl in the presence of $PPhMe_2$ provided an independent route to phenyl compound **12**, as determined by ^1H and $^{31}P\{^1H\}$ NMR spectrometry (eq 14).

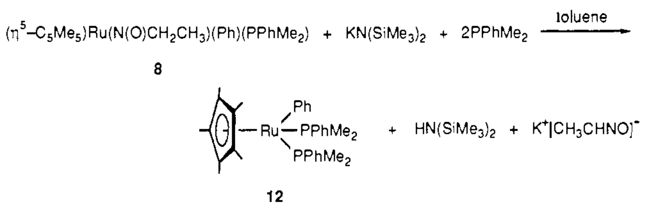
$$8 + CH_3CH_2MgCl \xrightarrow{+PPhMe_2} \underset{\mathbf{12}}{(\eta^5\text{-}C_5Me_5)Ru(Ph)(PPhMe_2)_2} \qquad (14)$$

Treatment of **8** with 1:1 $KN(SiMe_3)_2$/18-crown-6 produced an immediate color change from dark red to bright yellow. Spectrometric analysis showed a single major product (78%). This material was too sensitive to survive isolation; on the basis of partial spectrometric data we believe it is potassium ruthenate salt **13** (eq 15). At ambient temperature, the material darkened and

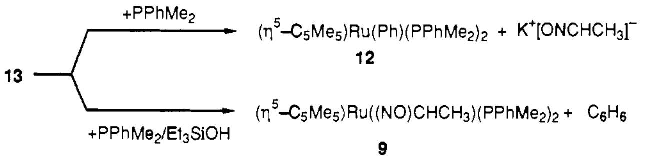
$$8 + KN(SiMe_3)_2 + 18\text{-Crown-6} \longrightarrow$$
$$\underset{\mathbf{13}}{[Crown \cdot K^+][(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PPhMe_2)(Ph)]^-} + HN(SiMe_3)_2 \qquad (15)$$

decomposed over several hours. The ^1H NMR spectrum showed a new C_5Me_5 resonance coupled to one phosphorus atom (δ 1.89 (d, 15 H, $J_{HP} = 1.2$ Hz) ppm) along with three methyl doublets. On the basis of these data, compound **13** is formulated as $[(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(Ph)(PPhMe_2)]^-K^+\cdot$18-crown-6.

Scheme II



Scheme III



The precise bonding mode of the oximate ligand is unknown.

The chemistry of **13** is consistent with this structural formulation, and with its viability as the initial product in the reaction of **8** with bases (Scheme III). Treatment of a solution of **13** with $PPhMe_2$ led to the immediate and quantitative formation of phenyl compound **12** and presumably $KONCHCH_3\cdot$18-crown-6. When **13** is instead treated with $PPhMe_2$ and a proton source (Et_3SiOH), the major organometallic product formed is oximate complex **9** (95%) along with a small amount of phenyl complex **12**. Attempts to trap **13** with an electrophilic alkylating agent to generate a ruthenium(IV) compound led only to intractable products.

Mechanistic Studies Employing Deuterium-Labeled 8. In order to explore the mechanism of the reaction of compound **8** with bases, the compounds $(\eta^5\text{-}C_5Me_5)Ru(N(O)CD_2CD_3)(Ph)(PPhMe_2)$ (**8**-d_5) and $(\eta^5\text{-}C_5Me_5)Ru(N(O)CD_2CD_3)(Ph\text{-}d_5)(PPhMe_2)$ (**8**-d_{10}) were prepared (Scheme IV). Treatment of phenyl(chloro) complex **5** with CD_3CD_2MgBr yielded after column chromatography 65% of complex **6**-d_5, characterized by IR, ^1H, and ^2H NMR spectrometry. Thermolysis of **6**-d_5 with $PPhMe_2$ in benzene at 85 °C gave **8**-d_5 in 51% yield. Compound **8**-d_5 was characterized by IR, ^1H, ^2H, and $^{31}P\{^1H\}$ NMR spectrometry. The reaction of dichloride complex **1** with C_6D_5MgBr and HCl gave 37% isolated yield of complex **5**-d_5; treatment of **5**-d_5 with CD_3CD_2MgBr gave **6**-d_{10} in 67% isolated yield. Both compounds were characterized by IR, ^1H, and ^2H NMR spectrometry. Thermolysis of complex **6**-d_{10} gave **8**-d_{10}, characterized by IR, ^1H, ^2H, and $^{31}P\{^1H\}$ NMR spectrometry, in 73% yield after workup.

Complex **8**-d_5 was treated with $NaOSiMe_3$ and $PPhMe_2$ in toluene at 60 °C for 12 h. The reaction mixture was separated into nonvolatile and volatile components. Spectrometric analysis of the nonvolatile components showed the formation of $(\eta^5\text{-}C_5Me_5)Ru((NO)CDCD_3)(PPhMe_2)_2$ (**9**-d_4) (88%) and a small amount of phenyl complex **12** (12%). Analysis by GC/MS of the volatile components showed a ratio of 33% C_6H_5D/67% C_6H_6 had been formed. The analogous reaction with complex **8**-d_{10} produced 90% **9**-d_4. Analysis of the volatile materials showed a 37% C_6D_6/63% C_6D_5H ratio. As a control, **8** was treated with $NaOSiMe_3$ and $PPhMe_2$ in toluene in the presence of excess CH_3OD; GC/MS analysis of the volatile components gave benzene with a 53% C_6H_5D/47% C_6H_6 ratio.

Kinetics of the Base-Catalyzed Conversion of 8 to 9. The Me_3SiONa-catalyzed conversion of nitrosoethyl complex **8** to oximate complex **9** was monitored by UV–visible spectrometry. In toluene at 60 °C, clean first-order plots of ln $(A - A_\infty)$ versus time were obtained. Under these conditions, the rate was found to be independent of $PPhMe_2$ concentration (Table IV, experiments 1–5). A simple rate order for $NaOSiMe_3$ could not be firmly established, most likely because of complications from aggregation effects upon the concentration of the active catalyst.

In an attempt to minimize these problems, an equivalent of 18-crown-6 was added to the reaction mixtures. This was found to greatly increase reaction rates. Kinetic runs were conducted at 25 °C with lower silanolate concentrations; clean first-order plots were obtained. While the observed rate constants (k_{obs})

Scheme IV

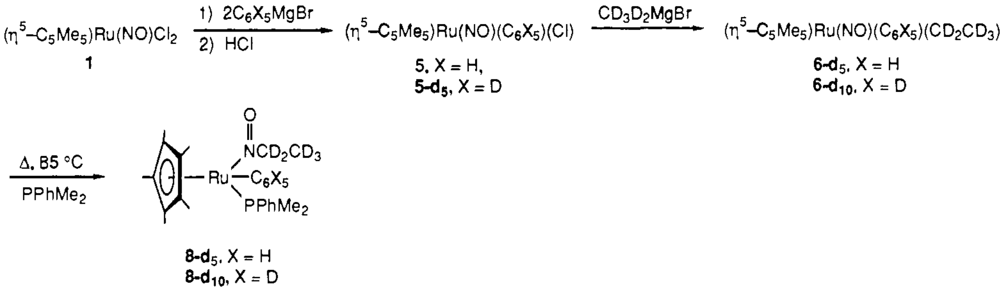


Table IV. First-Order Rate Constants for Silanolate-Catalyzed Reaction of $(\eta^5\text{-}C_5Me_5)Ru(N(O)CX_2CX_3)(Ph)(PPhMe_2)$ (**8**, X = H, D) + $PPhMe_2$

expt no.	X	10^4[**4**], M	[$NaOSiMe_3$], M	[18-crown-6], M	[$PPhMe_2$], M	temp, °C	k_{obsd},[a] s^{-1}
1	H	1.25	2.61×10^{-2}		3.60×10^{-3}	60	9.1×10^{-5}
2	H	1.25	2.61×10^{-2}		1.45×10^{-3}	60	8.8×10^{-5}
3	H	1.25	2.61×10^{-2}		3.36×10^{-2}	60	9.2×10^{-5}
4	H	1.25	2.61×10^{-2}		3.60×10^{-4}	60	9.1×10^{-5}
5	H	1.25	2.61×10^{-2}		6.37×10^{-3}	60	9.0×10^{-5}
6	H	1.65	2.14×10^{-3}	2.47×10^{-3}	7.09×10^{-3}	25	2.0×10^{-4}
7	H	1.65	3.92×10^{-3}	4.31×10^{-3}	5.79×10^{-3}	25	3.1×10^{-4}
8	H	1.25	7.07×10^{-3}	7.16×10^{-3}	3.43×10^{-3}	25	5.0×10^{-4}
9	H	1.25	1.20×10^{-2}	1.22×10^{-2}	2.57×10^{-3}	25	7.9×10^{-4}
10	H	1.25	1.45×10^{-2}	1.63×10^{-2}	3.43×10^{-3}	25	9.5×10^{-4}
11	H	1.23	4.75×10^{-3}	7.66×10^{-4}	2.42×10^{-3}	25	5.5×10^{-5}
12	H	1.23	4.75×10^{-3}	2.33×10^{-3}	2.42×10^{-3}	25	2.0×10^{-4}
13	H	1.23	4.77×10^{-3}	4.88×10^{-3}	2.17×10^{-3}	25	3.7×10^{-4}
14	H	1.23	4.72×10^{-3}	1.19×10^{-2}	2.17×10^{-3}	25	6.4×10^{-4}
15	H	1.23	4.72×10^{-3}	2.35×10^{-2}	2.17×10^{-3}	25	9.0×10^{-4}
16	H	1.23	4.77×10^{-3}	4.74×10^{-2}	2.17×10^{-3}	25	1.4×10^{-3}
17	D	0.921	4.72×10^{-3}	1.19×10^{-2}	2.42×10^{-3}	25	5.0×10^{-5}
18	D	3.25	4.72×10^{-3}	1.19×10^{-2}	4.34×10^{-3}	25	5.2×10^{-5}
19	D	3.25	4.72×10^{-3}	4.92×10^{-3}	4.34×10^{-3}	25	3.1×10^{-5}

[a] All values ±10%.

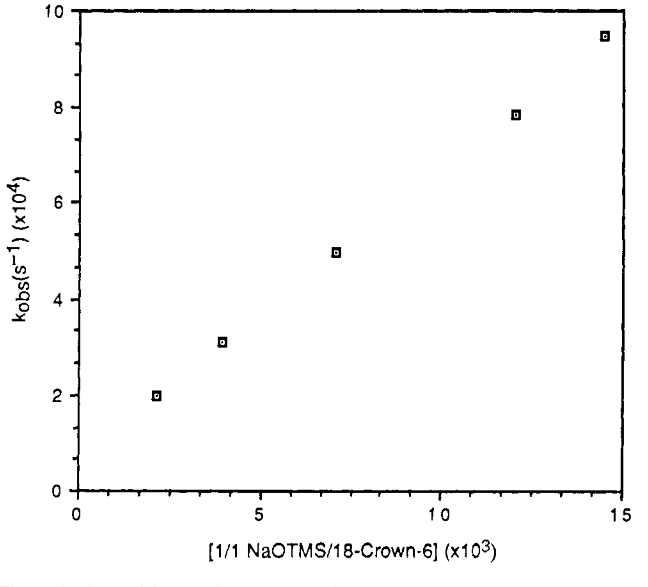


Figure 2. Plot of k_{obs} vs the concentration of a 1:1 mixture of $NaOSiMe_3$ and 18-crown-6 in the conversion of **8** to **9**.

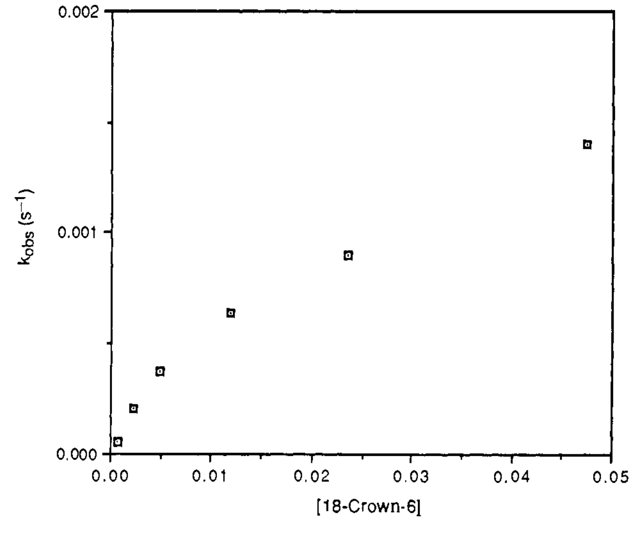


Figure 3. Plot of k_{obs} vs [18-crown-6] at constant [$NaOSiMe_3$] in the conversion of **8** to **9**.

Table V. Rate Data for DBU-Catalyzed Conversion of **8** to **9** at 65 °C

[**8**], M	[$PPhMe_2$], M	[DBU], M	k_{obsd},[a] s^{-1}	k_r, M^{-1} s^{-1}
1.44×10^{-4}	5.79×10^{-3}	0.0606	3.62×10^{-5}	6.0×10^{-4}
1.44×10^{-4}	5.79×10^{-3}	0.1142	7.00×10^{-5}	6.1×10^{-4}
1.44×10^{-4}	5.79×10^{-3}	0.2194	1.36×10^{-4}	6.2×10^{-4}

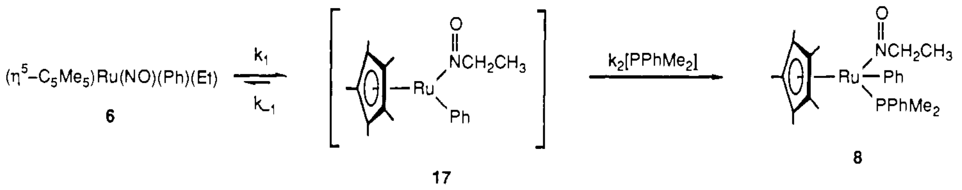
[a] All values ±10%.

increased with greater $NaOSiMe_3$/18-crown-6 concentrations (Table IV, experiments 6–10) (Figure 2), the order in catalyst concentration was still not an integral value. Variation of the 18-crown-6 concentration with a constant $NaOSiMe_3$ concentration produced a corresponding variation in k_{obs} (Table IV, experiments 11–16) (Figure 3). This is presumably due to a shift in the equilibrium between the sodium-uncomplexed and the sodium-complexed silanolate; the Na^+-complexed species serves as a much more active catalyst.

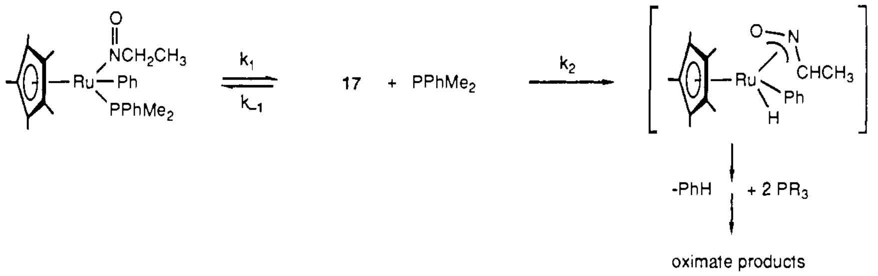
The rate of reaction of **8**-d_5 was measured at two different silanolate/18-crown-6 catalyst concentrations used previously with **8** (Table IV, experiments 17–19). Direct comparison revealed a very large deuterium isotope effect: $k_H/k_D = 12.3 \pm 0.3$.

The problems with aggregation were finally avoided by utilizing the non-ionic compound 1,8-diazabicyclo[5.4.0]undec-7-ene

Scheme V



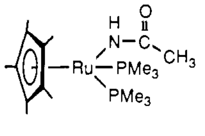
Scheme VI



(DBU) as the basic catalyst. While the reaction in the presence of DBU was much slower than that with $NaOSiMe_3$ (see Experimental Section), reasonable rates of the conversion of **8** to **9** were obtained by using higher catalyst concentrations at 65 °C in toluene. Clean first-order plots were obtained; the data clearly show a first-order dependence on DBU concentration (Table V).

Thermolysis of Ruthenium Oximate Complex 4. Thermolysis of diethyl ruthenium complex **2b** in the presence of PMe_3 at a higher temperature (125 °C), or alternatively thermolysis of oximate **4** at 75 °C for 4.5 h in benzene, led to an isomeric yellow material (eq 16). This material is obtainable in 35% isolated yield

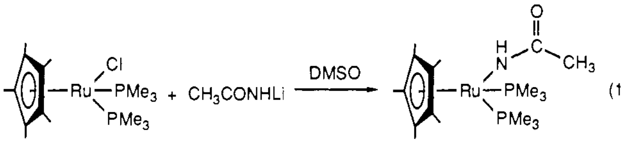
$$\underset{\mathbf{4}}{(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PMe_3)_2} \xrightarrow[C_6H_6]{\Delta,\ 75\ ^\circ C}$$



(16)

14

after recrystallization; it exhibits a ^1H NMR signal at δ 2.82 which disappears on treatment of the complex with D_2O. On the basis of spectrometric and analytical data, the product is assigned as the *N*-ruthenamide[16] complex **14**. Confirmation of this assignment was obtained by independent synthesis of **14** from $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and $CH_3CONHLi$ in DMSO (eq 17). Some $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH$ (vide infra) is also produced in this reaction.



(17)

14

The transformation of **4** to **14** is strongly inhibited by added phosphine. Furthermore, if $PPhMe_2$ is added instead of PMe_3, phosphine substitution is observed before isomerization.

In order to gain more information about possible intermediates involved in the transformation of **4** to **14**, $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NCCH_3)][PF_6]$ (**15**)[17] was prepared from $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and KPF_6 in CH_3CN (eq 18) (see Experimental Section). Treatment of acetonitrile complex **15** with $NMe_4OH{\cdot}5H_2O$ at 75 °C in benzene-d_6 gave complex **14** as the major product by ^1H NMR spectrometry (eq 19). Alternatively, $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH$ (**16**)[12] was prepared from $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and LiOH in DMSO (eq 20). No reaction of hydroxide complex **16** with CH_3CN in benzene-d_6 was observed after 15 h at 100 °C.

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl + KPF_6 \xrightarrow{CH_3CN} \underset{\mathbf{15}}{[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NCCH_3)]^+PF_6^-} \quad (18)$$

$$\mathbf{15} + NMe_4OH{\cdot}5H_2O \xrightarrow[C_6D_6]{\Delta,\ 75\ ^\circ C} \underset{\mathbf{14}}{(\eta^5\text{-}C_5Me_5)Ru(NHCOCH_3)(PMe_3)_2} \quad (19)$$

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl + LiOH \xrightarrow{DMSO} \underset{\mathbf{16}}{(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH} + LiCl \quad (20)$$

Discussion

Nitric Oxide Migratory Insertion of 6 in the Presence of PPhMe$_2$. The migratory insertion of NO into a ruthenium alkyl bond was proposed as a vital step in the thermal reactions of $(\eta^5\text{-}C_5Me_5)Ru(NO)R_2$ ($R = CH_3, CH_2CH_3$).[9] The phenyl-ethyl complex **6** undergoes analogous chemistry; its reaction with $PPhMe_2$ has allowed the isolation of the initial insertion product **8**, verifying this proposed step. Stable insertion products are not observed with the dialkyl analogues regardless of the phosphine employed. The kinetic data for the formation of compound **8** are consistent with a mechanism involving rate-determining migratory insertion to give a coordinatively unsaturated (or solvated) intermediate **17** followed by rapid trapping by $PPhMe_2$ (Scheme V). Deinsertion to regenerate **6** is apparently not competitive with trapping in the phosphine concentration range used. This mechanism is exactly analogous to the NO migratory insertion reactions of $(\eta^5\text{-}C_5H_5)Co(NO)(R)$ with PPh_3 and $(\eta^5\text{-}C_5R_5)Fe(NO)(CH_3)_2$ ($R = H, CH_3$) with PMe_3.[3]

Reactivity of Nitrosoalkyl Complexes. Ruthenium nitrosoalkyl insertion products are presumably formed in all these cases prior to further reaction. The process by which complex **8** is transformed into oximate compounds can be taken as a specific example. One initially plausible mechanism is outlined in Scheme VI. Reversible loss of $PPhMe_2$ would lead to intermediate **17** which subsequently rearranges via a β-elimination/reductive elimination sequence. The observation of substitution by PMe_3 prior to rearrangement demonstrates the lability of the $PPhMe_2$ ligand, supporting this route. A rate expression for this mechanism can be derived for this mechanism by applying the steady state approximation to intermediate **17** to give the rate law shown in eq 21. This would predict an inverse dependence of rate on $PPhMe_2$ concentration. However, this is inconsistent with the

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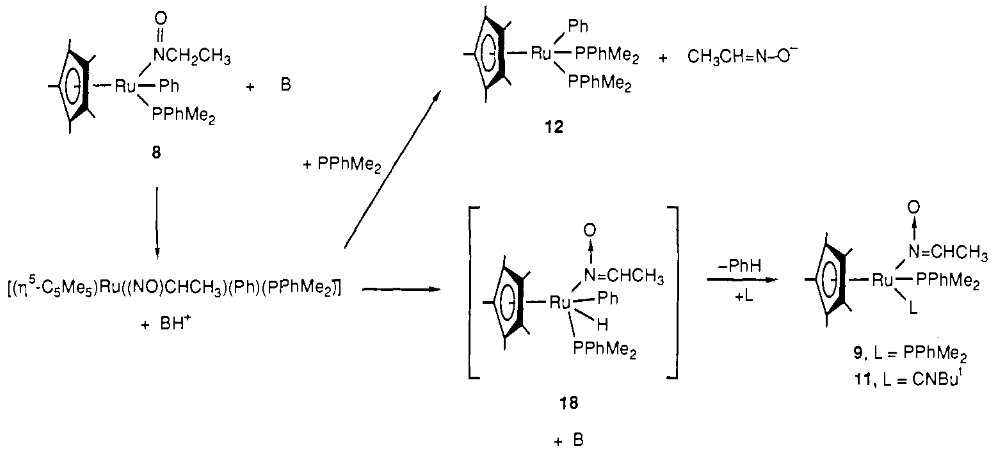
[16] Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley & Sons, Inc.: New York: 1980; Chapter 5.

[17] The BF_4^- salt has also been prepared: personal communication from J. E. Bercaw and R. A. Paciello.

Scheme VII



qualitative observation that the rate of conversion of compound **8** to compound **9** increases with greater [$PPhMe_2$]; hence, a mechanism involving initial dissociation of phosphine is discounted.

$$\text{Rate} = \frac{k_1 k_2 [\mathbf{8}]}{k_{-1}[\mathrm{PPhMe_2}] + k_2} \tag{21}$$

The phosphine dependence requires the rate-accelerating involvement of free phosphine in the rate law. One possible option would involve a phosphine-induced η^5 to η^3 interconversion ("ring slip")[18] of the C_5Me_5 ligand. This would give either direct dependence of k_{obs} on [$PPhMe_2$] or saturation in [$PPhMe_2$]. The subsequent loss of benzene in either case is more difficult to explain.

These mechanistic ambiguities were resolved by studying the treatment of nitrosoethyl complex **8** with bases stronger than phosphine in the presence of a trapping ligand. The data from these experiments allow us to propose the mechanism illustrated in Scheme VII. The initial, rate-determining step involves base abstraction of a methylene proton on the nitrosoethane ligand to generate an anionic ruthenium compound. This compound can be spectrometrically observed as its 18-crown-6 adduct **13** in the absence of a reactive partner. If a proton source is available (e.g., Me_3SiOH or H_2O), the proton is donated to the metal center to generate intermediate **18**. Loss of benzene and trapping by L then gives the oximate compounds **9** and **11**. If the conjugate acid formed in the initial step is very weak (e.g., $HN(SiMe_3)_2$) and no other source of protons is readily available, the incoming ligand L displaces the oximate as a salt, leading to **12**.

The proposed initial step is generally supported by the rate data for the base-catalyzed conversion of **8** to **9**, a bimolecular step that is first order in **8** and the base catalyst. The step involves the cleavage of a C–H bond. This predicts a primary isotope effect upon substitution of deuterium at the methylene carbon of the nitrosoethane moiety. The observed value of 12.3 ± 0.3 is well within the range for a primary isotope effect,[19] though it cannot be separated from possible contributing secondary isotope effects. In the formation of the η^1-oximate compounds, it is easiest to imagine that the loss of benzene occurs through the mediation of the ruthenium center. We therefore suggest a hydride intermediate (**18**) is formed by donation of a proton to the metal. The proton abstracted by the base is donated to regenerate the catalyst; however, our labeling studies indicate that adventitious proton sources could also form the proposed ruthenium hydride intermediate **18**. This mechanism is also consistent with the retention of the $PPhMe_2$ ligand in the coordination sphere of the metal.

In the case of $KN(SiMe_3)_2$ or CH_3CH_2MgCl, a proton cannot be readily donated to the metal center. The favored route available to the unstable anion appears to be displacement of the stable oximate anion to form the bis(phosphine)phenyl compound **12**.

In summary, the conversion of insertion compound **8** to oximate complexes is initiated by base abstraction of the acidic methylene proton of the nitrosoethyl group. Though the initial insertion products are not observed directly, the thermal reactions of the compounds $(\eta^5\text{-}C_5Me_5)Ru(NO)(R)(R')$ (R, R′ = CH_3, CH_3CH_2; R = CH_3, R′ = C_6H_5[15]) most likely occur through a similar mechanism with PMe_3 serving as the base. The lack of observation of insertion products where R = CH_3 may be attributed to the higher temperatures necessary for methyl migration; the subsequent reaction of the insertion product may be a much faster process. It should be noted that although the ruthenium center stabilizes the nitrosoethane ligand in complex **8**, the β-protons remain quite acidic.[20]

Formation of Cyanide Complex 3 and *N*-Ruthenamide Complex 14. A plausible mechanism by which complexes **3** and **14** are formed is outlined in Scheme VIII. Reversible interconversion of the N- and C-bound oximate complexes **4** and **19** could occur thermally on phosphine loss in **4**, consistent with the observed dissociative character of the conversion of **4** to **14**. As **19** is a ruthenium-substituted nitrosoalkane, it should undergo rapid prototropic isomerization to the corresponding oxime complex **20**, as is typical for this class of compounds. When R = H, elimination of H_2O leads to the isolated cyanide complex **3**. When R = CH_3, this elimination is prevented, and we suggest that the ruthenium analogue of a Beckmann rearrangement[21] converts oxime **20** to **21**. Complex **21** should quickly rearrange to its more stable isolable carboxamide tautomer **14**.

Since the oximate and carboxamide groups contain the elements of hydroxide and acetonitrile, complexes of these potential ligands might be considered as intermediates in the transformation of **4** to **14**. If this were the case, one might expect acetonitrile complex **15** to react with hydroxide anion to produce either **4** or **14**. As predicted, the observed product is **14**; it is formed at a rate fast enough for the reaction to be considered a reasonable mechanistic step, particularly in the conversion of **20** to **21** (R = CH_3). This metal-mediated hydrolysis of acetonitrile is a well-precedented process[22] and makes all the more plausible the analogy to the Beckmann rearrangement. Typically in the rearrangement of

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(18) See, for example: (a) Kershner, D. L.; Rheingold, A. L.; Basolo, F. *Organometallics* **1987**, *6*, 196–198. (b) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460–2461. (c) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329–331. (d) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912 and references therein.

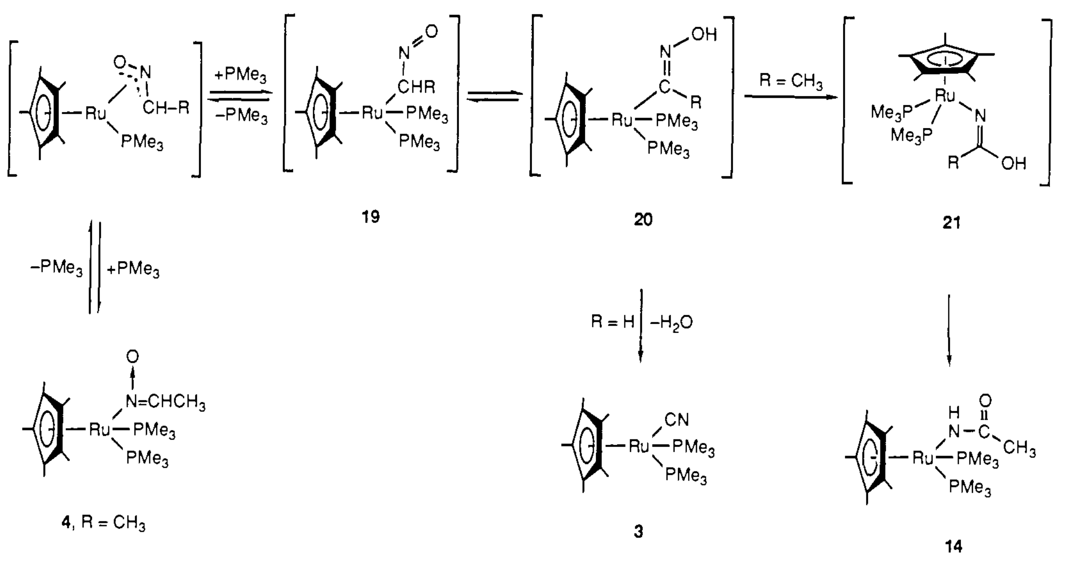
(19) (a) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; John Wiley & Sons, Inc.: New York: 1980. (b) Collins, C. J.; Bowman, N. S., Eds. *Isotope Effects in Chemical Reactions*; Van Nostrand Reinhold Company: New York: 1970; ACS Monograph 167.

(20) The Brønsted acidity of formaldoxime was shown to be substantially increased by coordination to $(\eta^5\text{-}C_5H_5)Cr(NO)_2{}^+$: Legzdins, P.; Richter-Addo, G. B.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1987**, *6*, 1807–1809.

(21) March, J. *Advanced Organic Chemistry—Reactions, Mechanisms and Structure*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1985; Chapter 8.

(22) Storhoff, B. N.; Huntley, C. L., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1–29.

Scheme VIII



oximes to amides,[21] the group trans to the hydroxyl migrates to nitrogen when hydroxide is converted to a better leaving group by a strong Lewis acid. Water then attacks at the other end of the carbon nitrogen multiple bond. For **20** it is reasonable that a strong Lewis acid is not needed, because the cationic fragment left when hydroxide dissociates is a stable acetonitrile complex. Furthermore, the attack of hydroxide at carbon now leads to the expected carboxamide structure. In any case, reaction of **15** with hydroxide represents an independent synthesis of **14**.

The insertion of organonitriles into the metal–oxygen bond of coordinated hydroxide ion has also been proposed as a possible mechanistic step in the formation of transition-metal carboxamide complexes.[22] However, hydroxide complex **16** does not react with acetonitrile, even at temperatures higher than those at which **14** was originally prepared. Thus, **16** is unlikely to be an intermediate in the conversion of **4** to **14**.

The apparent preference in this ruthenium system for the N-bound structure over the isomeric C-bound structure is unusual for late-transition-metal complexes. However, we note that the stability of oximate compound **4** over the unobserved isomer **19** parallels the stability of acetaldoxime over nitrosoethane; hence similar factors that account for the relative stabilities of organic oximes versus nitrosoalkanes may be operating in this ruthenium system.[23]

Experimental Section

General. All manipulations were conducted under nitrogen or argon with standard drybox, Schlenk, or vacuum line techniques, unless otherwise indicated. Experiments conducted in the drybox utilized a recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 or -2 Dri-Train and equipped with a −30 °C freezer.

Infrared (IR) spectra were recorded on either a Perkin-Elmer Model 283 grating spectrometer or a Perkin-Elmer Model 1550 Fourier transform spectrometer equipped with a Model 7500 Professional Computer. Gas chromatographic (GC) analyses were performed on either a Perkin-Elmer Sigma 3 gas chromatograph, connected to a Houston Instruments Omni Scribe recorder and using a 9 ft × $^1/_8$ in. stainless steel column packed with porapak Q, or a Hewlett-Packard 5890 gas chromatograph equipped with a Model 3396A integrator, and using a J&W Scientific DB5-60N 0.25 μm fused silica capillary column. Quantitative GC analyses used corrected detector responses. UV–visible measurements were conducted on a Hewlett-Packard 8450A spectrophotometer equipped with a Model 89100A temperature controller.

^{1}H NMR spectra were obtained at ambient temperature on a Bruker AM500, AM400 or on 200-, 250-, and 300-MHz instruments assembled by Rudi Nunlist at the University of California, Berkeley (UCB), NMR facility. Chemical shifts are reported in units of parts per million (ppm) (δ) downfield from tetramethylsilane (TMS). ^{1}H NMR shifts are relative to residual protiated solvent: benzene-d_5, δ 7.15; $CDHCl_2$, δ 5.32. ^{13}C NMR spectra were recorded at 75.5, 100.60, or 125.76 MHz and chemical shifts are reported relative to the solvent resonance: benzene-d_6, δ 128.00; CD_2Cl_2, δ 53.80. ^{31}P{^{1}H} NMR spectra were recorded at 121.5 MHz and chemical shifts are given relative to external 85% H_3PO_4. ^{2}H{^{1}H} NMR were recorded at 46.08 MHz and referenced to benzene-d_6. All coupling constants are reported in hertz. "Virtual triplets" (vt) refer to non-first-order multiplets that resemble triplets; the apparent coupling constant given is the separation between the two largest peaks.

Mass spectra were obtained at the UCB mass spectrometry facility on AEI MS-12 and Finnigan 4000 mass spectrometers. Elemental analyses were performed by the UCB microanalytical laboratory. Melting points were recorded in sealed capillary tubes under nitrogen on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Sealed NMR tubes were prepared by connection to Cajon Ultra Torr SS-6-UT-4 $^3/_8$ to $^1/_4$ in. reducing unions fitted with Kontes K-826500 high-vacuum Teflon stopcocks (referred to as "Cajon adapters"). The tubes were subsequently degassed and flame-sealed. "Glass bombs" refer to cylindrical, medium-walled Pyrex vessels joined to Kontes K-826510 high-vacuum Teflon stopcocks. Gas-phase mass measurements were performed by measuring the pressure in calibrated known-volume bulbs with a MKS Baratron connected to a high-vacuum line. Column chromatography was performed with silica gel (230–400 mesh ASTM, EM Reagents).

Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used without further purification. Pentane and hexane were distilled from $LiAlH_4$, and CH_2Cl_2 and CH_3CN from CaH_2, under nitrogen. Benzene, toluene, xylene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Methanol was distilled from Mg and vacuum transferred prior to use. Benzene-d_6 and CD_2Cl_2 were dried as their protiated analogues and vacuum transferred prior to use. Dimethyl sulfoxide (DMSO) was predried over CaH_2 and vacuum distilled. Lithium amide and triphenylmethane were added, and the DMSO was vacuum transferred from this mixture.

Trimethylphosphine (PMe_3) was purchased from Strem, dried over 1:5 Na:K alloy, and utilized exclusively by vacuum transfer. Dimethylphenylphosphine ($PPhMe_2$) was purchased from Strem and distilled from Na under vacuum. 18-Crown-6 was recrystallized from acetonitrile and dried by exposure to high vacuum overnight. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU) was distilled from BaO onto activated 4Å molecular sieves. Acetamide was recrystallized from boiling benzene and deprotonated with lithium diisopropyl amide in THF, from which the lithium salt precipitated. The $LiNHCOCH_3$ was washed free of excess acetamide with Et_2O and the remaining solvent removed under vacuum. CD_3CD_2MgBr and d_5-PhMgBr were prepared from Mg and the corresponding bromides (Cambridge Isotope Laboratories); the resultant solutions were titrated with 2-propanol with 5-methyl-1,10-phenanthroline as an indicator. NOCl was prepared from thionyl chloride and isoamyl nitrite according to the method of Stryker and Stork.[24] Chlorination of

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(23) (a) Adeney, P. D.; Bouma, W. J.; Radom, L.; Rodwell, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 4069–4074 and references therein. (b) Frost, D. C.; Lau, N. M.; McDowell, C. A.; Westwood, N. P. C. *J. Phys. Chem.* **1982**, *86*, 3577–3581 and references therein.

(24) Stryker, J. M. Ph.D. Dissertation, Columbia University, New York, New York, 1983.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(CO)}_2]_2$ to give $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(CO)}_2\text{Cl}$ was carried out by a modification of the procedure of Heinekey and Graham.[10] $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(PMe}_3)_2\text{Cl}$ was prepared by using the published procedure.[13]

$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(NO)Cl}_2$ (1). A 500-mL round-bottom flask equipped with a magnetic stir bar was charged with 2.67 g (8.14 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(CO)}_2\text{Cl}$ and stoppered with a Suba seal rubber septum. The flask was flushed with nitrogen via needles through the septum, and 300 mL of dry CH_2Cl_2 was added via cannula. The yellow solution was cooled in a dry ice/acetone bath. NOCl was allowed to bubble through the solution as it was being generated (from 2.0 mL (27 mmol) of thionyl chloride and 2.0 mL (15 mmol) of isoamyl nitrite). After stirring for 30 min, the reaction mixture was allowed to warm to room temperature and stirring was continued for 46 h, after which time no increase in product was detected by TLC (5% acetone in $\text{CH}_2\text{Cl}_2/\text{SiO}_2$). The reaction mixture was exposed to air, and the volatile materials were removed by rotary evaporation. The residue was purified by chromatography on silica gel (7 × 5 cm). A yellow band ($(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(CO)}_2\text{Cl}$) was eluted with CH_2Cl_2, followed by a dark green band with 5% acetone in CH_2Cl_2, which was concentrated by rotary evaporation. Recrystallization from a minimum amount of boiling toluene gave 1.46 g (53%) of dark green crystals: mp 250 °C dec; IR (CH_2Cl_2) $\nu_{\text{NO}} = 1790\ \text{cm}^{-1}$; ^{1}H NMR ($\text{CDCl}_3$) δ 1.84 (s, 15 H); ^{13}C NMR (CDCl_3) δ 9.50 (q, $J_{\text{CH}} = 130.1$ Hz, $\text{C}_5\textit{Me}_5$), 110.76 (q, $^2J_{\text{CH}} = 4.0$ Hz, $\textit{C}_5\text{Me}_5$); MS (EI), *m/e* 337 (M^+), 271 (base). Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{NORu}$: C, 35.62; H, 4.48; N, 4.15; Cl, 21.03. Found: C, 35.90; H, 4.50; N, 4.13; Cl, 21.41.

$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(NO)(CH}_3)_2$ (2a). A 125-mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 0.500 g (1.48 mmol) of **1** and 50 mL of toluene. The flask was equipped with a 50-mL pressure-equilizing addition funnel which was charged with 0.80 mL of AlMe_3 (2 M in toluene) which was diluted with toluene to make 10 mL of solution. The AlMe_3 solution was added dropwise over 30 min to the dark green slurry of **1**. After stirring for an additional 45 min, the reaction mixture was filtered through silica which was washed with toluene until the filtrate was colorless. The combined filtrates were concentrated under vacuum, and the residue was purified by sublimation at 60 °C and 10^{-4} Torr to give 0.295 g (67%) of red-orange solid **2a**: mp 76.5–77.5 °C; IR (benzene-d_6) $\nu_{\text{NO}} = 1735\ \text{cm}^{-1}$; ^{1}H NMR (benzene-$d_6$) δ 0.87 (s, 6 H), 1.38 (s, 15 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene-d_6) δ –0.50 ($\textit{C}\text{H}_3$), 9.08 ($\text{C}_5\textit{Me}_5$), 101.32 ($\textit{C}_5\text{Me}_5$); MS (EI), *m/e* 297 (M^+), 44 (base). Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{NORu}$: C, 48.63; H, 7.14; N, 4.72. Found: C, 48.84; H, 7.34; N, 4.69.

$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(NO)(CH}_2\text{CH}_3)_2$ (2b). A 200-mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 0.700 g (2.08 mmol) of **1** and 100 mL of toluene. The flask was equipped with a 50-mL pressure-equilizing addition funnel which was charged with 1.50 g of AlEt_3 (25% in toluene) which was diluted with toluene to make 10 mL of solution. The AlEt_3 solution was added dropwise over 20 min to the dark green slurry of **1**. After an additional 45 min of stirring, the reaction mixture was filtered through silica which was washed with toluene until the filtrate was colorless. The combined filtrates were concentrated under vacuum, and the residue was purified by sublimation of 50 °C and 10^{-4} Torr to give 0.378 g (56%) of red-orange solid **2b**: mp 48–50 °C; IR (benzene-d_6) $\nu_{\text{NO}} = 1720\ \text{cm}^{-1}$; ^{1}H NMR (benzene-$d_6$) δ 1.43 (s, 15 H), 1.59 (m 1 H), 1.72 (t, 3 H, $J = 7.1$ Hz), 1.82 (m, 1 H); ^{13}C NMR (benzene-d_6) δ 9.22 (q, $J_{\text{CH}} = 127.2$ Hz, $\text{C}_5\textit{Me}_5$), 18.07 (br t, $^1J_{\text{CH}} = 135.0$ Hz, $\textit{C}\text{H}_2\text{CH}_3$), 20.21 (q, $^1J_{\text{CH}} = 127.2$ Hz, $\text{CH}_2\textit{C}\text{H}_3$), 101.74 (br s, $\textit{C}_5\text{Me}_5$); MS (EI), *m/e* 325 (M^+), 59 (base). Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{NORu}$: C, 51.83; H, 7.77; N, 4.32. Found: C, 52.09; H, 7.79; N, 4.13.

Thermolysis of 2a with PMe_3. A 25-mL glass bomb equipped with a magnetic stir bar was charged with 108 mg (0.364 mmol) of **2a** and 5 mL of benzene. The mixture was degassed and 1.00 mmol of PMe_3 added by vacuum transfer. The reaction mixture was heated under vacuum by immersion in an oil bath at 150 °C for 20 h. During this time, the reaction mixture changed from deep red-orange to yellow-orange. After cooling to ambient temperature, the volatile materials were vacuum transferred to another bomb. GC/MS analysis of the volatile materials revealed the presence of large amounts of methane and water.

The nonvolatile product was purified by recrystallization from 2:1 v/v pentane/toluene at –40 °C, yielding 77.5 mg (51%) of yellow crystals of **3**: mp 180 °C dec; IR (KBr) $\nu_{\text{CN}} = 2060\ \text{cm}^{-1}$; ^{1}H NMR (benzene-$d_6$) δ 1.16 (vt, 18 H, $^2J_{\text{HP}} + {}^4J_{\text{HP}} = 8.4$ Hz), 1.66 (t, 15 H, $J_{\text{HP}} = 1.4$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene-d_6) δ 11.40 ($\text{C}_5\textit{Me}_5$); 21.76 (vt, $^1J_{\text{CP}} + {}^3J_{\text{CP}} = 28.7$ Hz, $\text{P}\textit{Me}_3$), 92.02 ($\textit{C}_5\text{Me}_5$), 142.74 (t, $^2J_{\text{CP}} = 21.1$ Hz, $\textit{C}\text{N}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene-d_6) δ 7.2; MS (EI), *m/e* 416 (M^+), 69 (base). Anal. Calcd for $\text{C}_{17}\text{H}_{33}\text{NP}_2\text{Ru}$: C, 49.26; H, 8.02; N, 3.38. Found: C, 49.59; H, 8.18; N, 3.41.

In order to determine the yield of volatile products in this reaction, a 5-mL glass bomb equipped with a magnetic stir bar was charged with 34.7 mg (0.117 mmol) of **2a**. Benzene (1.0 mL) and PMe_3 (0.348 mmol) were added by vacuum transfer after making sure they were degassed with 3 freeze–pump–thaw cycles. The frozen reaction mixture was evacuated thoroughly again before melting. The reaction mixture was heated as before for 20 h at 150 °C. The flask was opened to a system of four U-traps cooled in pentane/liquid nitrogen slush baths (–131 °C), and the non-condensible material was collected with a Toepler pump. The gas collected (218 Torr, 10.0 mL at 298 K; 0.117 mmol, 100%) was sampled directly and was shown to contain only methane by gas chromatography. The majority of the gas was condensed into a glass bomb at –196 °C and was confirmed to be methane by electron impact mass spectrometry. The materials that were condensed at –131 °C were vacuum transferred to a glass bomb. CD_3CN (1.0 mL) and dioxane (0.0318 mmol) were added by vacuum transfer. An aliquot of this mixture was removed in the drybox. A ^{1}H NMR spectrum was recorded and integrated. From the relative intensities of the water and dioxane signals the yield of water produced was calculated to be 0.12 mmol (100%).

Independent Synthesis of 3. A 50-mL two-neck round-bottom flask equipped with a magnetic stir bar and a stopper in one of the necks was charged with 114 mg (0.269 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(PMe}_3)_2\text{Cl}$ and 189 mg (2.90 mmol) of KCN. The flask was fitted with a vacuum stopcock and 20 mL of methanol was added by vacuum transfer. The reaction mixture was sampled by removing the stopper under a counterflow of argon in order to monitor the reaction by TLC ($\text{Et}_2\text{O}/\text{SiO}_2$). No more $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(PMe}_3)_2\text{Cl}$ remained after 10 min at ambient temperature and the mixture was pale yellow. After 20 min, the solvent was removed under vacuum. In the drybox, the residue was extracted with 25 mL of benzene, leaving a white powder. The benzene solution was concentrated under vacuum to give 101 mg (91%) of pale yellow solid. This material was found to be identical to **3** by ^{1}H, $^{13}\text{C}\{^1\text{H}\}$ NMR, and IR spectrometry.

Thermolysis of 2b with PMe_3. A 25-mL glass bomb equipped with a magnetic stir bar was charged with 0.281 g (0.866 mmol) of **2b** and 10 mL of benzene. PMe_3 (2.38 mmol) was vacuum transferred in. The bomb was immersed in an oil bath at 85 °C, and the reaction mixture was stirred under vacuum for 19 h. During this time period, the reaction mixture initially darkened, and then slowly turned yellow. After cooling to ambient temperature, the volatile materials were vacuum transferred to another bomb. GC/MS analysis of the volatile materials revealed a large amount of ethane generated.

The nonvolatile product was purified by recrystallization from 4:1 v/v pentane/toluene at –40 °C, which gave 0.292 g (76%) of yellow crystals of **4**: mp 150 °C dec; IR (KBr) 2975 (m), 2960 (m), 2910 (s), 2860 (m), 1737 (vw), 1653 (vw), 1542 (vw), 1519 (vw), 1481 (w), 1454 (w), 1431 (m), 1384 (s), 1373 (w), 1315 (vw), 1302 (w), 1292 (m), 1278 (m), 1150 (vw), 1103 (vw), 1066 (w), 1053 (m), 1036 (s), 957 (s), 940 (s), 852 (w), 710 (m), 665 (m), 571 (vw), 375 (w), 333 (vw) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.28 (vt, 18 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz), 1.55 (t, 15 H, $J_{HP} = 1.4$ Hz), 2.17 (d, 3 H, $J_{\text{HH}} = 5.2$ Hz), 6.43 (q, 1 H, $J_{\text{HH}} = 5.2$ Hz); ^{13}C NMR (benzene-d_6) δ 11.08 (q, $J_{\text{HP}} = 126.1$ Hz, $\text{C}_5\textit{Me}_5$), 15.62 (qd, $J_{\text{CH}} = 126.2$, 10.4 Hz, $\text{(NO)CH}\textit{C}\text{H}_3$), 20.68 (br q, $^1J_{\text{CH}} = 126.0$ Hz ($^1J_{\text{CP}} + {}^3J_{\text{CP}} = 26.7$ Hz), $\text{P}\textit{Me}_3$), 89.67 (br s, $\textit{C}_5\text{Me}_5$), 140.53 (dq, $^1J_{\text{CH}} = 126.2$ Hz, $^2J_{\text{CH}} = 10.4$ Hz, $\text{(NO)}\textit{C}\text{HCH}_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene-d_6) δ 4.3; MS (Cl, CH_4), *m/e* 446 ($\text{M}^+ - 1$), 371 (base). Anal. Calcd for $\text{C}_{18}\text{H}_{37}\text{NOP}_2\text{Ru}$: C, 48.42; H, 8.35; N, 3.14. Found: C, 48.67; H, 8.28; N, 3.04.

In order to determine the yield of volatile products in this reaction, a 5-mL glass bomb equipped with a magnetic stir bar was charged with 32.4 mg (0.0999 mmol) of **2b**. Benzene (1.0 mL) and PMe_3 (0.431 mmol) were added by vacuum transfer and were thoroughly degassed as in the thermolysis of **2a**. The reaction mixture was heated as before for 20 h at 85 °C. After cooling to ambient temperature, the gaseous products were separated by allowing the volatile materials in the reaction mixture to transfer into a system of four U-traps cooled in pentane/liquid nitrogen slush baths (–131 °C). The gas collected (166 Torr, 10.0 mL at 291 K; 0.0915 mmol) was completely condensed into a glass bomb. The gas composition was determined and quantified by GC. Only ethane and ethylene were detected. Their absolute yields were 0.0822 mmol (82%) and 0.0092 mmol (9%), respectively. The identities of the gaseous products were confirmed by GC/MS.

$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(NO)(Ph)(Cl)}$ (5). A single-neck 250-mL round-bottom flask was loaded with 1.49 g (4.41 mmol) of **1** and 75 mL of 1:1 v/v

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(25) For a description of the X-ray diffraction and analysis protocols used, see: (a) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834–5846. (b) Roof, R. B., Jr. *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*; Publication LA-4038, Los Alamos Scientific Laboratory: Los Alamos, NM 1969. (c) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(26) Personal communication from J. E. Bercaw and R. A. Paciello.

THF/hexane and equipped with a magnetic stir bar. PhMgCl was added dropwise by syringe as a THF solution (5.0 mL; 10.0 mmol) with stirring. The green slurry turned dark red over the addition period. After 1.5 h, the mixture was filtered through silica gel and washed through with ether. The combined filtrates were placed into a 250-mL Schlenk flask and concentrated on a vacuum line. The red residue was then placed under an atmosphere of nitrogen, redissolved in deaerated acetone, and treated with 0.40 mL (4.8 mmol) of 12 M HCl (aq). After 7 min of stirring, the mixture was concentrated under vacuum leaving a dark brown residue. The residue was purified by column chromatography on silica gel (5 × 10 cm) in the air. Elution with CH_2Cl_2 gave a large dark red-brown followed by a dark green band of starting material. Concentration of the red band by rotary evaporation followed by exposure to high vacuum gave 1.29 g (77%) of compound **5** as dark red-brown crystals: mp, no detectable melting or decomposition to 240 °C; IR (C_6H_6) ν_{NO} = 1770 cm^{-1}; ^1H NMR (benzene-d_6) δ 1.21 (s, 15 H), 7.10 (m, 1 H), 7.20 (m, 2 H), 7.58 (m, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 9.62 ($C_5\mathit{Me}_5$), 108.98 (C_5Me_5), 124.96 (para), 128.46 (meta), 138.90 (ortho), 154.44 (ipso); MS (EI), *m/e* 379 (M^+), 349 (base). Anal. Calcd for $C_{16}H_{20}ClNORu$: C, 50.72; H, 5.32; N, 3.70. Found: C, 50.68; H, 5.33; N, 3.65.

(η^5-C_5Me_5)Ru(NO)(Ph)(CH_2CH_3) (6). A 250-mL round-bottom flask was loaded with 1.29 g of **5** and 75 mL of THF and equipped with a magnetic stir bar. To the stirring red-brown mixture was added 2.5 mL (3.75 mmol) of CH_3CH_2MgCl as an Et_2O solution dropwise by syringe over 15 min. The color of the mixture turned deeper red over the addition period. The mixture was allowed to stir for an additional 2 h, and then filtered through silica gel. After washing the silica gel with Et_2O until the filtrates were colorless, the combined filtrates were concentrated under vacuum leaving a dark red residue. The residue was purified by column chromatography on silica gel (2 × 7 cm), and a single fraction of product was eluted with benzene. Concentration of this fraction gave 0.880 g (69%) of **6** as dark red flakes: mp 94–96 °C; IR (C_6H_6) ν_{NO} = 1739 cm^{-1}; ^1H NMR (benzene-d_6) δ 1.36 (s, 15 H), 1.62 (t, 3 H, J_{HH} = 7.1 Hz), 1.72 (m, 1 H), 2.36 (m, 1 H), 7.13 (m, 1 H), 7.23 (m, 2 H), 7.36 (m, 2 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 9.47 ($C_5\mathit{Me}_5$), 20.41 ($\mathit{C}H_2CH_3$), 20.73 ($CH_2\mathit{C}H_3$), 103.46 (C_5Me_5), 123.77 (para), 128.00 (meta), 139.04 (ortho), 158.13 (ipso); MS (Cl; CH_4), *m/e* 374 (M^+ + 1), 343 (M^+ − NO, base). Anal. Calcd for $C_{18}H_{25}NORu$: C, 58.04; H, 6.77; N, 3.76. Found: C, 58.15; H, 6.87; N, 3.71.

Thermolysis of 6 with PMe_3. A NMR tube was loaded with 7.4 mg (0.0199 mmol) of **6** and 0.7 mL of benzene-d_6 and connected to a Cajon adapter. The tube was degassed with 3 freeze–pump–thaw cycles on the vacuum line and 0.0722 mmol of PMe_3 added by vacuum transfer. The tube was flame-sealed under vacuum, thawed, and heated at 85 °C for 2.25 h to produce (η^5-C_5Me_5)Ru(N(O)CH_2CH_3)(C_6H_5)(PMe_3) (**7**) along with **4**; partial ^1H NMR spectrum for **7**: δ 0.99 (d, 9 H, J_{HP} = 9.4 Hz), 1.51 (d, 15 H, J_{HP} = 1.1 Hz), 3.70 (m, 1 H), 3.90 (m, 1 H). Heating the tube for 17 h at 85 °C converted the mixture completely to oximate complex **4**.

(η^5-C_5Me_5)Ru(N(O)CH_2CH_3)(Ph)($PPhMe_2$) (8). A 50-mL glass bomb was loaded with 0.213 g (0.572 mmol) of **2**, 0.367 g (2.66 mmol) of $PPhMe_2$, and 25 mL of benzene. The mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles and then heated under vacuum for 5.5 h at 85 °C. During this time the solution changed color from red to dark brown. The reaction mixture was cooled to ambient temperature and concentrated under vacuum. The oily brown residue was purified by column chromatography on silica gel (2 × 7 cm). Elution with 20:1 v/v hexane/Et_2O removed several small fractions that were discarded. The product was eluted with 10:1 v/v hexane/Et_2O. The product fraction was concentrated under vacuum leaving a dark red oil. By several cycles of redissolving the oil in pentane and reconcentration, 0.223 g (76%) of **8** was obtained analytically pure as dark red microcrystals: mp 128–129 °C; IR (C_6H_6) 1349 (s), 1275 (s), 1233 (s), 908 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 1.20 (t, 3 H, J_{HH} = 7.2 Hz), 1.30 (d, 3 H, J_{HP} = 8.7 Hz), 1.46–1.47 (overlapping doublets, 18 H), 3.73 (dq, 1 H, J_{HH} = 7.2, 11.7 Hz), 3.86 (dq, 1 H, J_{HH} = 7.2, 11.7 Hz), 7.07 (m, 2 H), 7.09 (m, 3 H), 7.22 (m, 2 H), 7.26 (m, 1 H), 7.33 (m, 2 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 10.31 ($C_5\mathit{Me}_5$), 13.24 ($CH_2\mathit{C}H_3$), 15.06 (d, J_{CP} = 33.9 Hz, P–$\mathit{C}H_3$), 16.88 (d, J_{CP} = 29.4 Hz, P–$\mathit{C}H_3$), 82.96 ($\mathit{C}H_2CH_3$), 99.27 (d, J_{CP} = 2.1 Hz, C_5Me_5), 121.81, 127.26, 127.85, 129.19, 131.71 (d, J_{CP} = 9.9 Hz), 138.69 (d, J_{CP} = 39.1 Hz), 140.36 (d, J_{CP} = 2.6 Hz), 167.51 (d, J_{CP} = 19.1 Hz); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 29.07; MS (EI), *m/e* 511 (M^+), 76 (base); UV–vis (toluene) λ_{max} = 397 nm ($\epsilon = 4.77 \times 10^3\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{26}H_{36}NOPRu$: C, 61.16; H, 7.11; N, 2.74. Found: C, 60.97; H, 7.07; N, 2.71.

Crystal Structure of 8. Red, prismatic crystals of **8** were obtained by slow crystallization from pentane at −30 °C. Fragments cleaved from some of these crystals were mounted on glass fibers with polycyanoacrylate cement. Preliminary precession photographs indicated monoclinic Laue symmetry and yielded approximate cell dimensions.

Table VI. Crystal and Data Parameters for **8**[a,b]

(A) Crystal Parameters at T = 25 °C[a,b]

empirical formula: $RuPONC_{26}H_{36}$
A = 8.6946 (6) Å
b = 10.7493 (13) Å
c = 26.946 (3) Å
α = 90.0°
β = 95.73 (46)°
γ = 90.0°
V = 2505.9 (8) $Å^3$
size: 0.16 × 0.17 × 0.29 mm

space group: $P2_1/c$
formula weight = 510.6 amu
Z = 4
d(calc) = 1.35 g cm^{-3}
μ(calc) = 6.9 cm^{-1}

(B) Data Measurement Parameters

radiation: Mo Kα (λ = 0.71073 Å)
monochromator: highly-oriented graphite (2θ = 12.2)
detector: crystal scintillation counter, with PHA
reflections measured: $+h$, $+k$, $+/-l$
2θ range: 3→45°
scan type: ω
scan width: $\Delta\theta = 0.60 + 0.35 \tan\theta$
scan speed: 0.72→6.70 (θ, deg/min)
background: measured over 0.25($\Delta\theta$) added to each end of the scan
vertical aperature = 3.0 mm
horizontal aperture = 2.0 + 1.0 tan θ mm
no. of reflections collected: 3721
no. of unique reflections: 3263
intensity standards: (526), ($26\bar{6}$), ($3\overline{1}\overline{16}$); measured very 1 h of X-ray exposure time; over the data collection period no decrease in intensity was observed
orientation: three reflections were checked after very 200 measurements; crystal orientation was redetermined if any of the reflections were offset by more than 0.10° from their predicted positions; reorientation was not needed during data collection

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 26° and 30°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

The crystal used for data collection was then transferred to our Enraf-Nonius CAD-4 diffractometer[25] and centered in the beam. Automatic peak search and indexing procedures yielded the monoclinic reduced primitive cell. Inspection of the Niggli values[25b] revealed no conventional cell of higher symmetry. The final cell parameters and specific data collection parameters are given in Table VI.

The 3741 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation of ±1% for the average curve. No correction for absorption was applied. Inspection of the systematic absences indicated uniquely space group $P2_1/c$. Removal of systematically absent and reductant data left 3263 unique data.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.25 to 1.3 times the B_{eqv} of the atoms to which they were attached. They were included in the structure factor calculations but not refined.

The final residuals for 271 variables refined against the 2795 data for which $F^2 > 3\sigma(F^2)$ were R = 2.20%, wR = 2.98%, and GOF = 1.88. The R value for all 3263 data was 3.87%. Positional parameters and their esd's for heavy atoms are given in Table VII.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.02 in the last cycles of refinement. The analytical forms of the scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[25c]

Inspection of the residuals ordered in ranges of $\sin\theta/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.32 $e^-/Å^3$, and the lowest excursion −0.25 $e^-/Å^3$. There was no indication of secondary extinction in the high-intensity low-angle data.

Anisotropic thermal parameters and the positions and thermal parameters of the hydrogen atoms, least-squares planes, along with a listing of the values of F_o and F_c, are available as supplementary material.

Table VII. Positional Parameters and Their Estimated Standard Deviations for **8**

atom	x	y	z	B (Å^2)
Ru	0.12067 (2)	0.22951 (2)	0.38156 (1)	2.683 (4)
P	0.32036 (8)	0.33686 (7)	0.35207 (3)	3.35 (2)
O	0.3648 (2)	0.0589 (2)	0.36416 (8)	5.85 (6)
N	0.2233 (3)	0.0776 (2)	0.36718 (8)	3.81 (5)
C1	−0.0933 (3)	0.2777 (3)	0.4204 (1)	3.81 (6)
C2	−0.0629 (3)	0.3764 (3)	0.3882 (1)	3.34 (6)
C3	−0.0794 (3)	0.3275 (3)	0.33844 (9)	3.29 (6)
C4	−0.1230 (3)	0.2012 (3)	0.3407 (1)	3.64 (6)
C5	−0.1287 (3)	0.1692 (3)	0.3917 (1)	4.00 (6)
C6	−0.1059 (4)	0.2873 (4)	0.4758 (1)	5.88 (9)
C7	−0.0551 (4)	0.5120 (3)	0.4016 (1)	4.84 (7)
C8	−0.0803 (4)	0.4015 (3)	0.2912 (1)	4.86 (8)
C9	−0.1768 (4)	0.1227 (3)	0.2960 (1)	5.64 (8)
C10	−0.1922 (4)	0.0503 (4)	0.4114 (2)	6.54 (9)
C11	0.2537 (3)	0.2510 (3)	0.4502 (1)	3.22 (6)
C12	0.3299 (3)	0.1517 (3)	0.4748 (1)	4.25 (7)
C13	0.4211 (4)	0.1666 (3)	0.5200 (1)	5.28 (8)
C14	0.4398 (4)	0.2819 (3)	0.5415 (1)	4.98 (8)
C15	0.3642 (4)	0.3824 (3)	0.5189 (1)	4.59 (7)
C16	0.2724 (3)	0.3663 (3)	0.4741 (1)	3.94 (7)
C17	0.3464 (3)	0.3131 (3)	0.2862 (1)	3.68 (6)
C18	0.4523 (4)	0.3837 (4)	0.2626 (1)	5.50 (8)
C19	0.4683 (4)	0.3692 (4)	0.2125 (1)	6.57 (9)
C20	0.3817 (5)	0.2850 (4)	0.1855 (1)	6.9 (1)
C21	0.2774 (6)	0.2136 (4)	0.2075 (1)	7.7 (1)
C22	0.2608 (4)	0.2276 (3)	0.2579 (1)	5.57 (8)
C23	0.3058 (4)	0.5071 (3)	0.3541 (1)	5.28 (8)
C24	0.5163 (3)	0.3152 (4)	0.3820 (1)	5.32 (8)
C25	0.1357 (4)	−0.0398 (3)	0.3549 (1)	5.74 (9)
C26	0.1809 (6)	−0.1403 (4)	0.3900 (2)	11.5 (2)

Kinetics of the Thermolysis of 6 with $PPhMe_2$ in C_6D_6. Samples were prepared by flame-sealing under vacuum 5-mm NMR tubes previously loaded with the appropriate reagents. The tubes were heated in a factory-calibrated Neslab Exocal Model 251 constant temperature bath filled with Dow Corning 200 Silicone Fluid and frozen rapidly in ice water after removal from the bath. Typically, the reactions were monitored to greater than 3 half-lifes by ambient-temperature ^{1}H NMR spectrometry by integrating the C_5Me_5 proton resonances of **6** vs an internal standard of ferrocene. The spectra were taken with a single acquisition and double checked with a second acquisition after a delay of at least $10T_1$. All kinetic plots displayed excellent linearity with correlation coefficients of 0.994 or better.

Thermolysis of 8 with PMe_3. A NMR tube was loaded with 7.0 mg (0.0137 mmol) of **8** and 0.7 mL of benzene-d_6 and connected to a Cajon adapter; it was then degassed with 3 freeze–pump–thaw cycles on the vacuum line. The tube was charged with 0.0371 mmol of PMe_3 by vacuum transfer, flame-sealed under vacuum, and heated for 40 min at 100 °C. Analysis by ^{1}H NMR spectrometry showed the main product to be compound **7**. Heating for 24 h at 100 °C converted all the starting material. The major product (70%) was $(\eta^5\text{-}C_5Me_5)Ru((NO)CHCH_3)(PMe_3)_2$ (**4**).

Thermolysis of 8 with $PPhMe_2$. A NMR tube was loaded with 5.2 mg (0.0102 mmol) of **8**, 10.0 mg (0.0724 mmol) of $PPhMe_2$, 1.0 mg of ferrocene, and 0.7 mL of benzene-d_6. The tube was connected to a Cajon adapter, degassed on the vacuum line with 3 freeze–pump–thaw cycles, and flame-sealed under vacuum. ^{1}H NMR spectra taken before and after thermolysis of the tube at 85 °C for 17 days showed η^1-oximate complex **9** had been formed in 68% yield (by integration of the C_5Me_5 resonance vs ferrocene internal standard).

Reaction of 8 with $NaOSiMe_3$ in the Presence of $PPhMe_2$. A 40-mL glass bomb was loaded with 0.125 g (0.245 mmol) of **8**, 0.0508 g (0.368 mmol) of $PPhMe_2$, 2.0 mg (0.018 mmol) of $NaOSiMe_3$, and 5 mL of toluene. The mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles and then heated for 5 h at 60 °C. The dark red mixture turned bright yellow over this time. The solution was concentrated under vacuum, leaving a bright yellow oil. The oil was extracted with pentane and the extracts concentrated to ca. 5 mL. Cooling the concentrated solution to −30 °C deposited yellow microcrystals that were collected to give 0.117 g (83%) of **9**. A sample suitable for analysis was obtained by an additional crystallization: mp 121–123 °C; IR (C_6H_6) 3090 (w), 3033 (w), 2977 (w), 2911 (w), 1964 (w), 1820 (w), 1524 (w), 1476 (w), 1435 (w), 1287 (w), 1276 (w), 1097 (w), 1067 (m), 1036 (m), 938 (m), 903 (m), 745 (m), 701 (m), 681 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.42 (t, 15 H, $J_{HP} = 1.5$ Hz), 1.50 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz), 1.60 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz), 2.25 (d, 3 H, $J_{HH} = 5.3$ Hz), 6.68 (q, 1 H, $J_{HH} = 5.3$ Hz), 7.10 (m, 6 H), 7.58 (m, 4 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 10.41 ($C_5\mathit{Me}_5$), 15.36 ($(NO)CHCH_3$), 17.36 (vt, $^1J_{CP} + {}^3J_{CP} = 26.0$ Hz, P–CH_3), 20.03 (vt, $^1J_{CP} + {}^3J_{CP} = 27.1$ Hz, P–CH_3), 89.98 (C_5Me_5), 127.81 (meta), 128.65 (para), 131.99 (ortho), 142.55 (vt, $^1J_{CP} + {}^3J_{CP} = 36.8$ Hz, ipso), 143.10 ($(NO)CHCH_3$); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 15.87; MS (FAB, sulfolane), *m/e* 571 (M^+). Anal. Calcd for $C_{28}H_{41}NOP_2Ru$: C, 58.93; H, 7.24; N, 2.45. Found: C, 58.86; H, 6.95; N, 2.39.

To determine the yield of volatile products, a 20-mL glass bomb was loaded with 0.0165 g (0.0323 mmol) of **8**, 4.8 mg (0.043 mmol) of $NaOSiMe_3$, 0.0129 g (0.0934 mmol) of $PPhMe_2$, 0.0148 g (0.139 mmol) of *p*-xylene as internal standard, and 1.5 mL of toluene. The mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles and then heated under vacuum for 7 h at 45 °C. After cooling to ambient temperature, the volatile materials were vacuum transferred to a 25-mL round-bottom flask equipped with a vacuum stopcock. GC and GC/MS analysis indicated that 0.0294 mmol (0.91 equiv) of benzene had been produced.

Reaction of 8 with $NaOSiMe_3$ in the Presence of PMe_3. A NMR tube loaded with 6.1 mg (0.012 mmol) of **8**, 6.0 mg (0.054 mmol) of $NaOSiMe_3$, and ca. 0.7 mL of C_6D_6 was connected to a Cajon adapter. On the vacuum line, the tube was degassed with 3 freeze–pump–thaw cycles, 0.0244 mmol of PMe_3 was added by vacuum transfer, and the tube was flame-sealed under vacuum. The mixture was checked by ^{1}H NMR spectrometry and then heated at 45 °C. Complete reaction of **8** was observed by ^{1}H NMR spectrometry after 6 h; a 60:40 ratio of mixed bisphosphine complex **10** to **4** was present. After 24 h at 45 °C, the ratio of **10** to **4** had changed to 20:80. Spectrometric data for **10**: ^{1}H NMR (benzene-d_6) δ 1.23 (d, 9 H, $J_{HP} = 8.2$ Hz), 1.46 (t, 15 H, $J_{HP} = 1.5$ Hz), 1.63 (d, 3 H, $J_{HP} = 8.0$ Hz), 1.68 (d, 3 H, $J_{HP} = 8.1$ Hz), 2.21 (d, 3 H, $J_{HH} = 5.3$ Hz), 6.58 (q, 1 H, $J_{HH} = 5.3$ Hz), 7.0–7.2 (m), 7.6–7.8 (m); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 0.80 (d, $^2J_{PP} = 47$ Hz), 19.6 (d, $^2J_{PP} = 47$ Hz).

Thermolysis of 9 with PMe_3. A NMR tube charged with 5.6 mg (0.0098 mmol) of **9**, 0.0351 mmol of PMe_3, and ca. 0.7 mL of C_6D_6 was flame-sealed under vacuum as above. After an initial ^{1}H NMR spectrum was acquired, the tube was heated at 45 °C. Heating for 1.5 h produced a 70:30 ratio of **10** to **4** with only a trace of **9** present; a final ratio of 10:90 was reached after 24 h.

Reaction of 8 with $NaOSiMe_3$, 18-Crown-6, and $PPhMe_2$. A NMR tube was loaded with 5.6 mg (0.011 mmol) of **8**, 3.6 mg (0.032 mmol) of $NaOSiMe_3$, 7.4 mg (0.028 mmol) of 18-crown-6, 5.0 mg (0.036 mmol) of $PPhMe_2$, and ca. 0.7 mL of C_6D_6 and then capped. The dark red solution turned bright yellow over a 30-min span. ^{1}H and $^{31}P\{^1H\}$ NMR spectrometry showed oximate compound **9** as the sole organometallic product.

Reaction of 8 with $NaOSiMe_3$ in the Presence of $NCBu^t$. A 40-mL glass bomb was loaded with 0.117 g (0.229 mmol) of **8**, 3.0 mg (0.027 mmol) of $NaOSiMe_3$, and 7 mL of toluene. The reaction mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles, 0.365 mmol of $CNBu^t$ was added by vacuum transfer, and then the bomb was heated under vacuum at 60 °C for 7 h. During this time period the solution changed color from dark red to light yellow. After cooling to ambient temperature, the volatile materials were vacuum transferred to a round-bottom flask equipped with a vacuum stopcock. GC/MS analysis of the volatile materials showed benzene had been produced. The oily yellow residue which remained was taken into the drybox, extracted with pentane, and concentrated under vacuum to ca. 2 mL. Cooling to −30 °C gave 68.3 mg (58%) of bright yellow flakes. Further concentration of the mother liquors gave a second crop: at total of 88.7 mg (75%) of **11** was obtained: mp 124–126 °C; IR (C_6H_6) 2978 (m), 2947 (m), 2906 (m), 2031 (vs), 1526 (w), 1479 (m), 1457 (w), 1435 (w), 1368 (w), 1321 (w), 1270 (w), 1230 (w), 1212 (m), 1102 (m), 1069 (m), 1030 (w), 994 (w), 942 (w), 910 (m), 823 (w), 745 (w), 707 (w) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.09 (s, 9 H), 1.59 (d, 3 H, $J_{HP} = 9.1$ Hz), 1.69 (d, 15 H, $J_{HP} = 1.7$ Hz), 1.97 (d, 3 H, $J_{HP} = 9.8$ Hz), 2.27 (d, 3 H, $J_{HH} = 5.3$ Hz), 6.93 (q, 1 H, $J_{HH} = 5.3$ Hz), 7.13 (m, 1 H), 7.18 (m, 2 H), 7.89 (m, 2 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 9.99 ($C_5\mathit{Me}_5$), 14.56 (d, $J_{CP} = 25.6$ Hz, P–CH_3), 15.86 ($(NO)CHCH_3$), 17.95 (d, $J_{CP} = 29.8$ Hz, P–CH_3), 31.74 ($C(CH_3)_3$), 55.50 ($C(CH_3)_3$), 93.06 (d, $J_{CP} = 1.9$ Hz, C_5Me_5), 127.78 (d, $J_{CP} = 9.2$ Hz, meta), 129.02 (s, para), 132.04 (d, $J_{CP} = 10.5$ Hz, ortho), 140.00 (d, $J_{CP} = 37.9$ Hz, ipso), 140.77 ($(NO)CHCH_3$), 172.64 (d, $J_{CP} = 22.1$ Hz, $CNBu^t$); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 27.17; MS (FAB, sulfolane), *m/e* 516 (M^+). Anal. Calcd for $C_{25}H_{29}N_2OPRu$: C, 58.23; H, 7.62; N, 5.43. Found: C, 57.84; H, 7.49; N, 5.35.

To determine the yield of volatile materials in this reaction, 14.1 mg (0.0276 mmol) of **8**, 8.7 mg (0.078 mmol) of $NaOSiMe_3$, 18.8 mg (0.177 mmol) of *p*-xylene, and 1.5 mL of toluene was loaded into a 20-mL glass bomb. The mixture was degassed with 3 freeze–pump–thaw cycles on the vacuum line and 0.0351 mmol of $CNBu^t$ was added by vacuum transfer. The bomb was heated under vacuum at 45 °C for 12 h and brought to ambient temperature, and the volatile materials were vacuum transferred to a 25-mL round-bottom flask equipped with a vacuum stopcock. GC analysis of the volatile products showed 0.028 mmol (100%) of benzene had been formed.

Reaction of 8 with $KN(SiMe_3)_2$ in the Presence of $PPhMe_2$. A 50-mL round-bottom flask was loaded with 0.101 g (0.197 mmol) of **8** and 10 mL of toluene. To this stirred red solution was added $KN(SiMe_3)_2$ (0.0416 g; 0.243 mmol) and $PPhMe_2$ (0.460 g; 0.333 mmol) in ca. 5 mL of toluene. The solution turned bright yellow over 10 min. After an additional 2 h of stirring, the volatile materials were removed under vacuum. The oily yellow residue was extracted with 5:1 v/v pentane/toluene leaving behind 0.0145 g (76%) of $KONCHCH_3$ (identified by hydrolysis and comparison with a commercial sample of $HONCHCH_3$ by GC analysis and ^1H NMR spectrometry). The extracts were concentrated under vacuum and the residue purified by column chromatography on silica gel (2 × 7 cm). A single yellow fraction was removed with 5:1 v/v hexane/toluene and concentrated under vacuum to give 0.0997 g (86%) of phenyl compound **12** as bright yellow flakes; mp 151–152 °C; IR (C_6H_6) 2979 (w), 2916 (w), 1562 (w), 1479 (m), 1435 (w), 1375 (w), 1289 (w), 1276 (w), 1093 (w), 1012 (w), 934 (w), 900 (m), 829 (w), 744 (w), 732 (w), 706 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.28 (vt, 6 H, $^2H_{HP} + {}^4J_{HP} = 7.5$ Hz), 1.55 (t and vt, overlapped, 21 H), 6.74 (m, 3 H), 7.22 (m, 6 H), 7.38 (m, 4 H), 7.51 (m, 2 H); (C_6D_6) δ 1.25 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 7.3$ Hz), 1.46 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 7.1$ hz), 1.54 (t, 15 H, $J_{HP} = 1.2$ Hz), 7.02 (m, 6 H), 7.16 (m, 3H), 7.32 (m, 4 H), 7.79 (m, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 11.14 (C_5Me_5), 19.25 (vt, $^1J_{CP} + {}^3J_{CP} = 26.6$ Hz, P–CH_3), 21.45 (vt, $^1J_{CP} + {}^3J_{CP} = 26.4$ Hz, P–CH_3), 92.46 (C_5Me_5), 119.14 (para), 125.17 (meta), 127.63 (vt, $^3J_{CP} + {}^5J_{CP} = 7.8$ Hz, *m*-P), 128.49 (ortho), 132.10 (vt, $^2J_{CP} + {}^4J_{CP} = 10.2$ Hz, *o*-P), 142.47 (vt, $^1J_{CP} + {}^3J_{CP} = 34.1$ Hz, *ipso*-P), 145.82 (vt, $^4J_{CP} + {}^6J_{CP} = 9.1$ Hz, *p*-P), 169.88 (t, $J_{CP} = 14.9$ Hz, ipso); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 20.79; MS (FAB, sulfolane), *m/e* 590 (M^+). Anal. Calcd for $C_{32}H_{42}P_2Ru$: C, 65.18; H, 7.18; P, 10.50. Found: C, 65.04; H, 7.20; P, 9.96.

Reaction of 8 with CH_3CH_2MgCl in the Presence of $PPhMe_2$. A C_6D_6 solution of 4.2 mg (0.0082 mmol) of **8** and 5.0 mg (0.036 mmol) of $PPhMe_2$ was treated with an excess of an Et_2O solution of CH_3CH_2MgCl. The dark red solution immediately turned bright yellow. ^1H and $^{31}P\{^1H\}$ NMR analysis of the crude mixture showed phenyl complex **12** as the sole organoruthenium product.

Reaction of 8 with $KN(SiMe_3)_2$ and 18-Crown-6. A NMR tube was loaded with 7.5 mg (0.015 mmol) of **8**, 3.0 mg (.018 mmol) of $KN(SiMe_3)_2$, 4.4 mg (0.017 mmol) of 18-crown-6, 3.3 mg (0.018 mmol) of bibenzyl as internal standard, and ca. 0.7 mL of benzene-d_6. The red solution rapidly turned bright yellow; integration of the ^1H NMR spectrum showed 78% of **13** had been formed; partial spectrometric data for **13**: ^1H NMR (benzene-d_6) δ 1.89 (d, 15 H, $J_{HP} = 1.2$ Hz), 1.76 (d, 3 H, $J_{HP} = 8.2$ Hz), 1.81 (d, 3 H, $J_{HP} = 7.2$ Hz), 1.98 (d, 3 H, $J_{HH} = 5.3$ Hz), 3.17 (br s, 18-crown-6), 7.0–7.2 (m, 2 H), 7.2–7.4 (m, 5 H), 8.14 (m, 3 H); $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 26.54.

Reactions of 13 with $PPhMe_2$. Compound **13** was generated from 8.1 mg (0.16 mmol) of **8**, 3.5 mg (0.020 mmol) of $KN(SiMe_3)_2$, and 4.9 mg (0.019 mmol) of 18-crown-6 in ca. 0.7 mL of benzene-d_6 (2.9 mg (0.016 mmol) of bibenzyl was added as internal standard) and placed into a NMR tube. Integration of the ^1H NMR spectrum showed **13** as the major product (83%). To the solution was added 5.0 mg (0.036 mmol) of $PPhMe_2$. An immediate lightening of the solution was observed along with the formation of a white solid, presumably $[K^+\cdot crown][ONCHCH_3]^-$. ^1H and $^{31}P\{^1H\}$ NMR spectrometry showed that phenyl compound **12** was formed in quantitative yield from **13**.

Reaction of 13 with Et_3SiOH and $PPhMe_2$. In a similar manner, 8.3 mg (0.016 mmol) of **8**, 3.2 mg (0.019 mmol) of $KN(SiMe_3)_2$, 5.0 mg (0.019 mmol) of 18-crown-6, 3.4 mg (0.019 mmol) of bibenzyl as internal standard, and ca. 0.7 mL of benzene-d_6 were placed into a NMR tube; integration of the ^1H NMR spectrum showed **13** was formed in 73% yield. The tube was cooled to −30 °C in the drybox freezer and 10.0 μL (0.065 mmol) of Et_3SiOH and 5.0 mg (0.036 mmol) of $PPhMe_2$ were added. A quick but faint lightening of the solution was noted when the tube was thawed. ^1H NMR spectrometry showed 95% oximate complex **9** and 5% phenyl complex **12** had formed (based on **13**).

Synthesis of 5-d_5. In a similar manner to the preparation of **5**, 1.09 g (3.22 mmol) of dichloride complex **1** in 75 mL of THF was treated dropwise with an Et_2O solution of d_5-PhMgBr (6.50 mmol; 13.0 mL). Treatment with aqueous HCl followed by column chromatography gave 0.462 g (37%) of **5**-d_5 as dark red-brown flakes: IR (C_6H_6) $\nu_{NO} = 1770$ cm^{-1}; ^1H NMR (benzene-d_6) δ 1.27 (s, 15 H); $^2H\{^1H\}$ NMR (CH_2Cl_2) δ 7.10, 7.13.

Synthesis of 6-d_5 and 6-d_{10}. A 100-mL round-bottom flask loaded with 0.637 g (1.68 mmol) of **5** and 40 mL of THF was treated dropwise with an Et_2O solution of d_5-EtMgBr (0.80 mL; 1.76 mmol). After 4 h of stirring, the solution was concentrated under vacuum and the dark red residue purified by column chromatography on silica gel to give 0.413 g (65%) of **6**-d_5 as a red powder: IR (C_6H_6) $\nu_{NO} = 1738$ cm^{-1}; ^1H NMR (benzene-d_6) δ 1.37 (s, 15 H), 7.16 (m, 1 H), 7.21 (m, 2 H), 7.42 (m, 2 H); $^2H\{^1H\}$ NMR (C_6H_6) δ 1.53; 1.64, 2.27.

In an exactly analogous fashion, 0.212 g (0.552 mmol) of **5**-d_5 was treated with d_5-EtMgBr (0.30 mL; 0.66 mmol); workup by column chromatography gave 0.141 g (67%) of **6**-d_{10}: IR (C_6H_6) $\nu_{NO} = 1738$ cm^{-1}; ^1H NMR (benzene-d_6) δ 1.37 (s, 15 H); $^2H\{^1H\}$ NMR (C_6H_6) δ 1.51, 1.63, 2.25, 7.14, 7.23, 7.35.

Synthesis of 8-d_5 and 8-d_{10}. A 40-mL bomb was loaded with **6**-d_5 (0.173 g; 0.459 mmol), $PPhMe_2$ (0.410 g; 2.97 mmol), and 20 mL of benzene. The mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles and heated under vacuum for 6 h at 85 °C. The mixture was concentrated under vacuum and the dark brown oily residue was purified by column chromatography as for **8** to give 0.121 g (51%) of **8**-d_5: IR (C_6H_6) 1313 (s), 1277 (s), 909 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 1.31 (d, 3 H, $J_{HP} = 8.7$ Hz), 1.46 (d, 15 H, $J_{HP} = 1.2$ Hz), 1.49 (d, obscured, 3 H), 7.0–7.4 (m, 5 H); $^2H\{^1H\}$ NMR (C_6H_6) δ 1.11, 3.67, 3.78; $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 29.07.

In a similar fashion, 0.140 g (0.387 mmol) of **6**-d_{10} and 0.370 g (2.68 mmol) of $PPhMe_2$ in 20 mL of benzene was degassed and heated under vacuum for 6 h at 85 °C. Subsequent purification by column chromatography yielded 0.151 g (73%) of **8**-d_{10}: IR (C_6H_6) 1311 (s), 1276 (s), 1037 (s), 909 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 1.30 (d, 3 H, $J_{HP} = 8.7$ Hz), 1.46 (d, 15 H, $J_{HP} = 1.2$ Hz), 1.47 (d, 3 H, $J_{HP} = 9.3$ Hz), 7.70 (m, 3 H), 7.34 (m, 2 H); $^2H\{^1H\}$ NMR (C_6H_6) δ 1.15, 3.72, 3.78, 7.1–7.3; $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 29.11.

Reaction of 8-d_5 and 8-d_{10} with $NaOSiMe_3$ in the Presence of $PPhMe_2$. A 20-mL glass bomb was loaded with **8**-d_5 (15.7 mg; 0.0304 mmol), 2.0 mg (0.018 mmol) of $NaOSiMe_3$, 7.0 mg (0.051 mmol) of $PPhMe_2$, and 2.0 mL of toluene. The mixture was degassed on the vacuum line with 3 freeze–pump–thaw cycles then heated under vacuum at 60 °C for 12 h. The volatile materials were vacuum transferred into a 25-mL round-bottom flask equipped with a vacuum stopcock. GC/MS analysis of the volatile materials showed a 65/35 ratio of C_6H_6/C_6H_5D had been formed. The nonvolatile yellow residue was analyzed by NMR spectrometry; the major product (88%) was **9**-d_4: ^1H NMR (benzene-d_6) δ 1.41 (t, 15 H, $J_{HP} = 1.5$ Hz), 1.50 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz), 1.60 (vt, 6 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz), 7.10 (m, 6 H), 7.58 (m, 4 H); $^2H\{^1H\}$ NMR (C_6H_6) δ 2.15, 6.60; $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 15.89.

Similarly, 15.0 mg (0.0288 mmol) of **8**-d_{10}, 2.0 mg (0.018 mmol) of $NaOSiMe_3$, 6.0 mg (0.043 mmol) of $PPhMe_2$, and 2.0 mL of toluene were loaded into a 40-mL glass bomb that was then degassed and heated at 60 °C under vacuum for 12 h. The volatile materials were vacuum transferred to a round-bottom flask; GC/MS analysis showed a 63/37 ratio of C_6H_5D/C_6D_6 had been formed. Analysis of the nonvolatile materials by ^1H and $^{31}P\{^1H\}$ NMR spectrometry showed **9**-d_4 as the major product (90%).

The reaction of 15.2 mg (0.0298 mmol) of **8**, 2.0 mg (0.018 mmol) of $NaOSiMe_3$, 12.0 mg (0.0869 mmol) of $PPhMe_2$, 10.0 mg (0.587 mmol) of CH_3OD, and 2.0 mL of toluene was conducted as a control. After heating under vacuum at 60 °C for 12 h and vacuum transfer of the volatile materials, GC/MS analysis showed a 47/53 ratio of C_6H_6/C_6H_5D had been formed.

Rate of the Base-Catalyzed Conversion of 8 to 9 Monitored by UV-Visible Spectrometry. All solutions were prepared and stored in the drybox using volumetric flasks and freshly distilled toluene. Best results were obtained with fresh catalyst solutions. In a typical run, aliquots of the reagents were measured with volumetric pipets into one of a set of matched and previously balanced quartz spectrometer cells sealed to Kontes 826510 high-vacuum Teflon stopcocks and equipped with a small magnetic stir bar. The reaction vessel was then sealed and the contents thoroughly mixed and brought to temperature in the spectrometer. Reactions were typically monitored to greater than 3 half-lifes at 420 nm. Runs utilizing $NaOSiMe_3$ and 18-crown-6 are summarized in Table IV; runs with DBU are listed in Table V.

Thermolysis of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2((NO)CHCH_3)$ (4). Preparation of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NHCOCH_3)$ (14). A 25-mL flask was charged with 95.6 mg (0.214 mmol) of **4** and 5 mL of benzene. The flask was equipped with a magnetic stir bar and a vacuum stopcock and placed under an argon atmosphere on a vacuum line. The reaction mixture was heated at 75 °C for 4.5 h during which time the solution turned from yellow to yellow-orange. The solvent was removed under vacuum and the residue was recrystallized from 4:1 v/v pentane/toluene at −40 °C to give 34.9 mg (35%) of yellow crystalline **14**: mp 222 °C dec; IR (KBr) 3370 (m, sharp), 1593 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.18 (vt, 18 H, $^2J_{HP} + {}^4J_{HP} = 8.0$ Hz), 1.64 (t, 15 H, $J_{HP} = 1.5$ Hz), 2.17 (s, 3 H), 2.82 (br s, 1 H); ^{13}C NMR (benzene-d_6) δ 11.36 (q, $J_{CH} = 126.1$ Hz, $C_5\mathit{Me}_5$), 20.99 (br q, $J_{CH} = 126.0$ Hz ($^1J_{CP} + {}^3J_{CP} = 25.5$ Hz), $P\mathit{Me}_3$), 28.37 (q, $^1J_{CH} = 124.9$ Hz, $NH(CO)\mathit{C}H_3$), 89.14 (br s, C_5Me_5), 176.07 (br s, $NH(\mathit{C}O)CH_3$); ^{31}P{^{1}H} NMR (benzene-d_6) δ 5.3; MS (CI, CH_4), *m/e* 446 ($M^+ - 1$), 77 (base). Anal. Calcd for $C_{18}H_{37}NOP_2Ru$: C, 48.42; H, 8.35; N, 3.14. Found: C, 48.92; H, 8.56; N, 3.40.

Reaction of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl with $CH_3CONHLi$. A NMR tube attached to a ground glass joint was charged with 5.0 mg (0.012 mmol) of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl, 5.5 mg (0.085 mmol) of $CH_3CONHLi$, and 0.5 mL of DMSO-d_6. The tube was fitted with a vacuum stopcock, removed to a vacuum line, and flame-sealed under vacuum. The tube was heated to 50 °C and the reaction monitored by ^{1}H NMR spectrometry. During the course of the reaction, one major resonance each appeared for a new C_5Me_5 and PMe_3 ligand. After 1 h, the solution had turned from orange to pale yellow. The tube was broken open in the drybox and the mixture concentrated under vacuum. By ^{1}H and ^{31}P{^{1}H} NMR spectrometry, the major organometallic product (69%) was identified as **14**, and the other C_5Me_5 and PMe_3 containing product was identified as **16** (vide infra).

Inhibition of the Rearrangement of 4. A 1.00-mL solution of 17.5 mg (0.0392 mmol) of **4** in benzene-d_6 was prepared. A NMR tube attached to a ground glass joint was charged with 0.50 mL of this solution and fitted with a vacuum stopcock. PMe_3 (0.357 mmol) was added by vacuum transfer and the tube sealed. The remainder of the solution of **4** was placed into another NMR tube and sealed under vacuum. The reactions of both tubes were monitored by ^{1}H NMR spectrometry. After heating both tubes simultaneously at 100 °C for 15 min, no reaction was observed in the tube to which PMe_3 had been added. However, the tube without added phosphine no longer contained any **4**, and **14** was the major product.

Thermolysis of 4 with $PPhMe_2$. A NMR tube attached to a ground glass joint was loaded with 2.6 mg (0.0058 mmol) of **4**, 4.4 mg (0.032 mmol) of $PPhMe_2$, and 0.7 mL of benzene-d_6. The tube was topped with a vacuum stopcock and sealed off under vacuum. The reaction was monitored by ^{1}H NMR spectrometry while heating at 75 °C. After 90 min, a steady state was established in which the amount of **4** relative to **10** remained constant at a ratio of 1:1, in spite of the large excess of $PPhMe_2$ present. In addition, 1 equiv of free PMe_3 was produced. No **14** was observed by either ^{1}H or ^{31}P{^{1}H} NMR spectrometry.

[(η^5-C_5Me_5)Ru(PMe_3)$_2$($NCCH_3$)][PF_6] (15). A 50-mL round-bottom flask was charged with 0.435 g (1.03 mmol) of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl, 0.190 g (1.03 mmol) of KPF_6, and 25 mL of CH_3CN. After stirring for 24 h at ambient temperature, the solution had turned pale yellow and the precipitate which had formed was removed by suction filtration through Celite. The Celite was washed with CH_3CN until the filtrate was colorless. The combined filtrates were concentrated under vacuum to a volume of ca. 3 mL and 15 mL of Et_2O was added to precipitate 0.460 g (78%) of **15** as a yellow crystalline solid: mp 240 °C dec; IR (KBr) $\nu_{CN} = 2275$ cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.41 (vt, 18 H, $^2J_{HP} + {}^4J_{HP} = 8.4$ Hz), 1.68 (t, 15 H, $J_{HP} = 1.6$ Hz), 2.37 (t, 3 H, $J_{HP} = 1.6$ Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 4.24 ($NC\mathit{C}H_3$), 10.75 ($C_5\mathit{Me}_5$), 19.96 (vt, $^1J_P + {}^3J_{CP} = 29.2$ Hz, $P\mathit{Me}_3$), 91.22 (C_5Me_5), 125.06 ($NCCH_3$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −144.0 (septet, $J_{PF} = 711$ Hz), 1.0; MS (FAB, thioglycerol), *m/e* 430 (((η^5-C_5Me_5)Ru(PMe_3)$_2$($NCCH_3$)$^+$), 389 (base). Anal. Calcd for $C_{18}H_{36}F_6NP_3Ru$: C, 37.63; H, 6.32; N, 2.44. Found: C, 37.87; H, 6.49; N, 2.46.

Reaction of 15 with $Me_4NOH{\cdot}5H_2O$. A NMR tube attached to a ground glass joint was charged with 4.7 mg (0.0082 mmol) of **15** and 16.2 mg (0.0894 mmol) of $Me_4NOH{\cdot}5H_2O$. The tube was fitted with a vacuum stopcock and 0.7 mL of benzene-d_6 vacuum transferred in. The tube was sealed off and heated at 75 °C while monitoring the reaction by ^{1}H NMR spectrometry. After 28.5 h of heating, the major C_5Me_5 containing product (81%) was identified as **14**.

(η^5-C_5Me_5)Ru(PMe_3)$_2$OH (16). A 50-mL round-bottom flask was charged with 107 mg (0.252 mmol) of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl, 113 mg (4.72 mmol) of LiOH, and 10 mL of DMSO. The flask was equipped with a magnetic stir bar and a vacuum stopcock. After stirring for 17 h, the volatile materials were removed under vacuum. The crude product was redissolved in 5 mL of benzene in the drybox and filtered. The yellow precipitate was washed four times with 5 mL each of benzene and the benzene removed from the combined filtrates by lyophilization. A minimum of boiling pentane was used to redissolve the residue and then cooled to −40 °C to crystallize out 10.0 mg (10%) of yellow **16**: ^{1}H NMR (benzene-d_6) δ 1.57 (t, 15 H, $J_{HP} = 1.6$ Hz), 1.22 (vt, 18 H, $^2J_{HP} + {}^4J_{HP} = 8.2$ Hz); ^{31}P{^{1}H} NMR (benzene-d_6) δ 3.1 [lit.[12,26] ^{1}H NMR (benzene-d_6) δ 1.59 (t, 15 H, $J_{HP} = 1.5$ Hz), 1.22 (vt, 18 H, $^2J_{HP} + {}^4J_{HP} = 8.0$ Hz); ^{31}P{^{1}H} NMR (benzene-d_6) δ 3.096].

Attempted Reaction of 16 with CH_3CN. A NMR tube attached to a ground glass joint was charged with 2.5 mg (0.0062 mmol) of **16**, 2.0 μL (0.038 mmol) of CH_3CN, and 0.7 mL of benzene-d_6. The tube was fitted with a vacuum stopcock and sealed under vacuum. ^{1}H NMR spectra were recorded periodically while heating the tube. No reaction was observed after 15 h at 100 °C.

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Supplementary Material Available: Tables giving further details of the structure determination of complex **8** including temperature factor expressions (*B*'s), least-squares planes, and the positions and thermal parameters of the hydrogen atoms (6 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.