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# Reductive Elimination Leading to Transient ($\eta^5$-$C_5Me_5$)Ru(NO). Trapping, Dimerization, and Oxidative Addition Reactions of This Intermediate and the Effect of Structural Variation on Its Generation

**Jeffrey Chang and Robert G. Bergman***

*Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received January 26, 1987*

**Abstract:** The compound ($\eta^5$-$C_5Me_5$)Ru(NO)$Ph_2$ (**2**) was synthesized from ($\eta^5$-$C_5Me_5$)Ru(NO)$Cl_2$ (**1**) and PhMgCl. Heating **2** in benzene produces biphenyl and dimers [($\eta^5$-$C_5Me_5$)Ru($\mu$-NO)]$_2$ (**3**) and [($\eta^5$-$C_5Me_5$)Ru($\mu$-NO)(Ph)]$_2$ (**4**). Heating solutions of **2** at different concentrations or in different solvents changes the ratios of these products. Thermolysis in the presence of $CH_2Cl_2$ or $PR_3$ gives either the C-Cl insertion product ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_2Cl$)(Cl) (**5**) or ($\eta^5$-$C_5Me_5$)Ru(NO)($PR_3$) (**6a**, R = Ph; **6b**, R = Me), respectively. Compound **6b** and free $PMe_3$ exist in equilibrium with ($\eta^5$-$C_5Me_5$)Ru(NO)($PMe_3$)$_2$ (**7**), proposed to have a bent NO group. Heating **2** with 1,2-bis(dimethylphosphino)ethane (dmpe) gives the related complex ($\eta^5$-$C_5Me_5$)Ru(NO)(dmpe) (**8**), which in this case can be isolated. The thermal reactions of **2** with $CH_2Cl_2$ and $PR_3$ proceed at the same rate. In the case of $PPh_3$, the rate of reaction is first-order in **2** and zero-order in phosphine; its activation parameters are $\Delta H^{\ddagger} = 21.9 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -7 \pm 2$ eu. The data suggest that the various thermal reactions of **2** occur through a common intermediate, suggested to be ($\eta^5$-$C_5Me_5$)Ru(NO). The reaction of **1** with $CH_2$=CHMgBr gives ($\eta^5$-$C_5Me_5$)Ru(NO)($\eta^2$-butadiene) (**11**). The reaction of ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)$_2$ with HCl gives ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(Cl) (**12**). Compound **12** reacts with $CH_2$=CHMgBr or PhMgCl to give ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(CH=$CH_2$) (**13**) and ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(Ph) (**15**), respectively. Upon heating, **13** undergoes reductive elimination to give ($\eta^5$-$C_5Me_5$)Ru(NO)($\eta^2$-propene) (**14**) while **15** does not reductively eliminate under thermal conditions. The thermal reactivities of these compounds are discussed in terms of thermodynamic and kinetic influences upon reductive elimination.

The chemistry of transition-metal alkyl nitrosyl complexes has exhibited considerable variety. Legzdins and co-workers have prepared unusual 16-electron molybdenum and tungsten complexes, ($\eta^5$-$C_5H_5$)M(NO)$R_2$,[1] which display novel reactivity with oxygen[2] and sulfur.[3] Major efforts have been directed toward the discovery and understanding of the migratory insertion of NO into metal-carbon bonds; the formation of new carbon-nitrogen linkages and the general incorporation of nitrogen into organic groups are intriguing goals. Indirect and spectroscopic observation of NO insertion has been reported for a number of organo-transition-metal systems.[4] The alkylcobalt nitrosyl system of Weiner and Bergman,[5] ($\eta^5$-$C_5H_5$)Co(NO)R, is well-understood: it is the first well-studied system where the insertion of coordinated nitric oxide into transition-metal-alkyl bonds leads to simple, isolated nitrosoalkyl-metal complexes. Similar insertions of coordinated NO into the metal-alkyl bonds of ($\eta^5$-$C_5R_5$)Fe(NO)$Me_2$ (R = H, Me) have also been reported.[6] The known compound ($\eta^5$-$C_5H_5$)Cr(NO)$_2$Me[7] has recently been shown to insert external $NO^+$ to give an organometallic formaldoxime complex.[8] Diel[6b] has reported examples in the iron system ($\eta^5$-$C_5R_5$)Fe(NO)$R^1_2$ ($R^1$ = $CH_2C_6H_5$, $CH_2SC_6H_5$), which undergo reductive elimination to give the coupled organic products $R^1$-$R^1$ and the dimer [($\eta^5$-$C_5H_5$)Fe($\mu$-NO)]$_2$.

The pentamethylcyclopentadienyl ruthenium compounds ($\eta^5$-$C_5Me_5$)Ru(NO)$R_2$ (R = Me, Et), prepared by Seidler and Bergman,[9] were observed to undergo NO insertion into the metal-alkyl bonds as part of a complex transformation leading to various ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$X (X = CN, N(H)C(O)$CH_3$, ONCH$CH_3$) compounds. In seeking to understand the reactivity of the ruthenium system, we have synthesized and examined several new analogues of these complexes. In the systems to be discussed here, we have found chemistry characterized by reductive elimination, rather than by migratory insertion, leading to the generation of a variety of new ruthenium nitrosyl complexes.

## Results and Discussion

**Synthesis of ($\eta^5$-$C_5Me_5$)Ru(NO)$Ph_2$ (2).** Arylation at ruthenium in ($\eta^5$-$C_5Me_5$)Ru(NO)$Cl_2$ (**1**) was initially accomplished with triphenylaluminum; the arylation proceeds more cleanly and in higher yield using Grignard reagents. All other arylation reagents tried, including PhLi, did not produce the desired product. In a typical experiment, a hexane/THF (ca. 1:1 v/v) solution of dichloride **1** was treated with a slight excess of a THF solution of PhMgCl, causing a color change from dark green to deep red. Filtration through silica gel followed by crystallization afforded the desired product as analytically pure dark red crystals of diphenyl complex **2** in 65-74% yield (eq 1).

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2} + 2PhMgCl \longrightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5Me_5)Ru(NO)Ph_2} + 2MgCl_2 \qquad (1)$$

Complex **2** is an air-stable, nonvolatile solid and has been fully characterized by conventional spectroscopic methods and combustion analysis. The presence of a linear terminally bound NO ligand is indicated by an intense IR absorption at 1755 $cm^{-1}$ Resonances due to the $\sigma$-bound phenyl ligands are clearly visible in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra. Particularly revealing is the ipso-carbon resonance at $\delta$ 157.90 which is in the range of other ipso-carbon shifts of aryl ligands $\sigma$-bound to ruthenium.[10]

**Thermolysis of 2.** The thermal reactivity of diphenyl complex **2** is very different from its previously synthesized dimethyl and

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[1] Legzdins, P.; Rettig, S. J.; Sanchez, L.; Bursten, B. E.; Gatter, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411-1413.

[2] Legzdins, P.; Rettig, S. J.; Sanchez, L. *Organometallics* **1985**, *4*, 1470-1471.

[3] Legzdins, P.; Sanchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525-5526.

[4] 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.; Guastini, 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) Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880-1882. (i) Clement, R. A.; Klabunde, U.; Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 87-94.

[5] (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.

[6] (a) Seidler, M. D.; Bergman, R. G. *Organometallics* **1983**, *2*, 1897-1899. (b) Diel, B. N. *J. Organomet. Chem.* **1985**, *284*, 257-262.

[7] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38-45.

[8] Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 317-318.

[9] (a) Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6110-6111. (b) Seidler, M. D. Ph.D. Thesis, University of California, Berkeley, CA, 1984.

[10] Mann, B. E.; Taylor, B. F. *$^{13}C$ NMR Data for Organometallic Compounds*; Academic: New York, 1981.

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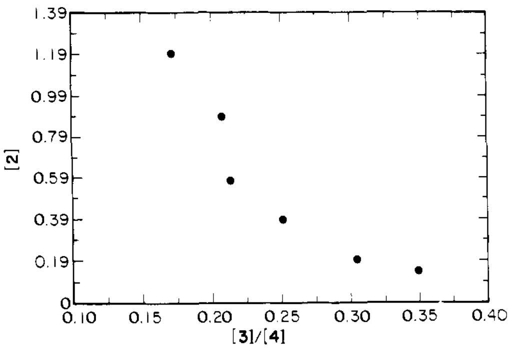
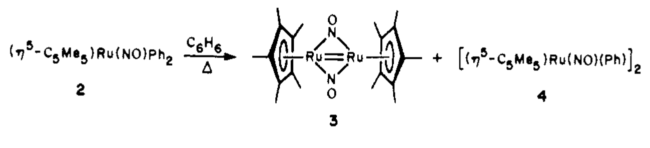


**Figure 1.** Plot of [**2**] vs. the ratio [**3**]/[**4**] over the course of the thermolysis of **2** in $C_6D_6$. Concentrations are relative numbers based on integration in the $^1$H NMR spectra versus an internal standard.

diethyl analogues. The latter dialkyl compounds are thermally robust; in solution they are stable to 130 and 85 °C respectively. They react at these temperatures in the presence of $PMe_3$ to produce cyano, carboxamide, or oximate bis(phosphine) complexes.[9] In contrast, thermolysis of **2** in benzene at 45 °C leads to the formation of biphenyl (identified by GC and $^1$H NMR comparison with an authentic sample) and two predominant organometallic products in ratios dependent on the reaction conditions (vide infra) (eq 2). The two organometallic products were

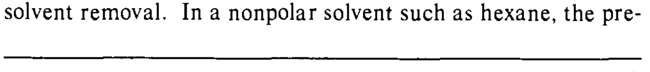


(2)

identified following separation by column chromatography and subsequent purification by recrystallization. One product is a bright red solid formulated as the dimer $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)]_2$ (**3**). Mass spectral data show a parent peak at *m/e* 534 ($M^+ + 1$). The IR spectrum displays a strong absorbance at 1535 cm$^{-1}$ ascribed to a bridging NO ligand.[11] $^1$H and $^{13}C\{^1H\}$ NMR spectroscopy show $C_5Me_5$ as the only carbon–hydrogen containing ligand. The assignment was supported by independent synthesis; the reduction of dichloride **1** with Zn/EtOH produced a compound spectroscopically identical with **3**.[12]

The other organometallic product was isolated as an air-stable deep purple solid which analyzed correctly for $C_{32}H_{40}N_2O_2Ru_2$. The mass spectrum shows a parent ion at *m/e* 687 ($M^+$). $^1$H and $^{13}C\{^1H\}$ NMR spectroscopy indicate only the presence of $C_5Me_5$ and $\sigma$-bound phenyl ligands. On the basis of these data and an IR band at 1497 cm$^{-1}$, the compound is formulated as the dimer $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)(Ph)]_2$ (**4**).

The relative ratio of the two metal-containing products depends on the concentration of **2** and the nature of the solvent. Qualitatively, in benzene, the ratio of **3** to **4** increases as the concentration of **2** decreases over the course of the thermolysis (Figure 1). Lowering the initial concentration of **2** also increases the ratio of **3** to **4** (Figure 2). In a polar, donating solvent such as EtOH or $CH_3CN$, the only products observed are dimer **3** and biphenyl (eq 3). Dimer **3** can be isolated from the reactions in donor solvents in quantitative yield (>97%). Although biphenyl was formed in quantitative yield as estimated by $^1$H NMR spectroscopy, only ca. 50% was isolated, presumably due to loss during solvent removal. In a nonpolar solvent such as hexane, the predominant organometallic product is diphenyl dimer **4** (ca. 80% by $^1$H NMR spectroscopy); concentration effects could not be examined quantitatively due to the limited solubility of **2** in aliphatic hydrocarbons. The two dimers are each stable at the reaction temperature; neither appears to form from the other.



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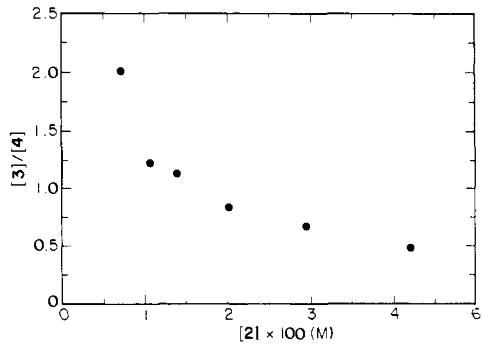
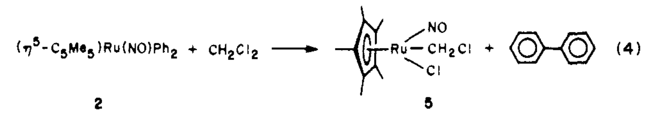


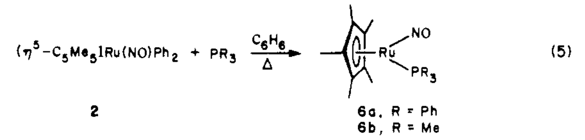
**Figure 2.** Plot of the final product ratios [**3**]/[**4**] vs. the initial concentrations of diphenyl complex [**2**] in the thermolysis of **2** in $C_6D_6$.

**Thermolysis with $CH_2Cl_2$.** When diphenyl monomer **2** is heated in neat $CH_2Cl_2$ or in benzene with ca. 10 equiv of $CH_2Cl_2$ at 45 °C, a new organometallic compound **5** is formed as the major product (70%) along with a moderate amount of dimer **3** (30%). Unfortunately, we were unable to completely purify **5**; identification is based on $^1$H and $^{13}C\{^1H\}$ NMR spectroscopy, IR spectroscopy, and mass spectrometry. Compound **5** is formulated as $(\eta^5\text{-}C_5Me_5)Ru(NO)(CH_2Cl)(Cl)$, the product resulting from insertion into the C–Cl bond (eq 4).[13] The $^1$H NMR spectrum of compound **5** displays an AB spin pattern ($\delta$ 3.88 ($J$ = 7.2 Hz), 5.94 ($J$ = 7.2)) attributed to the diastereotopic methylene protons. The $^{13}C\{^1H\}$ NMR spectrum shows a single carbon resonance in addition to those of the $C_5Me_5$ ligand. The IR spectrum shows a strong absorbance at 1771 cm$^{-1}$.



(4)

**Thermolysis in the Presence of Phosphines.** Thermolysis of diphenyl monomer **2** at 45 °C with an excess of $PR_3$ (R = Ph, Me) in benzene produces as the major isolable products the monophosphine adducts $(\eta^5\text{-}C_5Me_5)Ru(NO)(PR_3)$ (**6a**,**b**) (eq 5).



(5)

The $PPh_3$ analogue **6a** is produced in 70% yield ($^1$H NMR integration vs. ferrocene) but could only be isolated in poor yield (20%). In pure form, **6a** is a very air-sensitive dark yellow solid which is insoluble in aliphatic solvents but is quite soluble in aromatic solvents. In the $^1$H NMR spectrum, the $C_5Me_5$ protons appear as a doublet with $J_{HP}$ = 1 Hz, indicating the coordination of a single phosphine to the ruthenium center. The complex displays a strong absorbance at 1670 cm$^{-1}$ in the IR spectrum, which we attribute to a linear NO stretching absorption. Other spectroscopic and analytical data are consistent with this formulation.

The $PMe_3$ analogue was prepared similarly and was purified by recrystallization from pentane (36% yield). Isolated **6b** exists as dark red crystals which are very soluble in common organic solvents. In the $^1$H NMR spectrum, the $C_5Me_5$ signal again appears as a doublet with $J_{HP}$ = 1 Hz. The NO stretching absorption in the IR spectrum appears at 1647 cm$^{-1}$; the shift in

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(11) The parent cyclopentadienyl compound displays $\nu_{NO}$ = 1472 cm$^{-1}$: Herrmann, W. G.; Hubbard, J. L. *J. Organomet. Chem.* **1984**, *262*, C46–C50.

(12) The synthesis and partial characterization of **3** was initially accomplished by Mark D. Seidler in these laboratories.

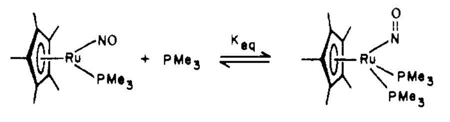
(13) For examples of related oxidative additions, see: (a) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630–634 and references therein. (b) Burns, E. G.; Chu, S. S. C.; deMeester, P.; Lattman, M. *Ibid.* **1986**, *5*, 2383–2384 and references therein.

Table I. Infrared N--O Stretching Frequencies

| compd | $\nu_{NO}$, cm$^{-1}$ |
|---|---|
| ($\eta^5$-$C_5Me_5$)Ru(NO)$Ph_2$ (**2**) | 1755 |
| [($\eta^5$-$C_5Me_5$)Ru($\mu$-NO)]$_2$ (**3**) | 1535 |
| [($\eta^5$-$C_5Me_5$)Ru($\mu$-NO)(Ph)]$_2$ (**4**) | 1497 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_2Cl$)(Cl) (**5**) | 1771 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($PPh_3$) (**6a**) | 1670 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($PMe_3$) (**6b**) | 1647 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)(dmpe) (**8**) | 1386 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($\eta^2$-$CH_2$=CHCH=$CH_2$) (**11**) | 1695 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(Cl) (**12**) | 1755 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(CH=$CH_2$) (**13**) | 1741 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($\eta^2$-$CH_2$=$CHCH_3$) (**14**) | 1692 |
| ($\eta^5$-$C_5Me_5$)Ru(NO)($CH_3$)(Ph) (**15**) | 1742 |

this band compared to that observed in the $PPh_3$ analogue is consistent with the greater electron-donating properties of $PMe_3$.

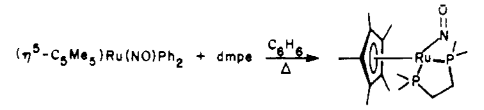
When the thermolysis of **2** with $PMe_3$ was monitored by $^1H$ NMR spectroscopy, another organometallic product was observed in addition to **6b**. Attempts to isolate this compound were unsuccessful. Spectroscopic evidence implicates the bis(phosphine) nitrosyl structure ($\eta^5$-$C_5Me_5$)Ru(NO)($PMe_3$)$_2$ (**7**) for this material.[14] In the $^1H$ NMR spectrum, a triplet at $\delta$ 1.76 (15 H, $J_{HP}$ = 1.0 Hz) and a "virtual triplet" at $\delta$ 0.87 (18 H, $^2J_{HP} + {}^4J_{HP}$ = 8.2 Hz) indicate the only proton-containing ligands to be $C_5Me_5$ and two $PMe_3$ groups; these ligands are also observed in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. In order to maintain an 18-electron configuration at the metal, the nitrosyl ligand presumably exists in a bent conformation, but the NO stretching absorption in the IR spectrum could not be unambiguously assigned. Our inability to isolate bis(phosphine) complex **7** was due to the fact that it is in rapid equilibrium with mono(phosphine) complex **6b** and $PMe_3$: removal of $PMe_3$ from **7** resulted in complete reversion to **6b** (eq 6). Addition of varying amounts of $PMe_3$ to **6b** allowed determination of $K_{eq}$ = 16 M$^{-1}$ at 20 °C.



(6)

**6b** **7**

In an effort to produce an isolable analogue of bent NO complex **7**, **2** was heated with an excess of 1,2-bis(dimethylphosphino)ethane (dmpe) in benzene at 45 °C. This led to the formation of dmpe complex **8** as the sole organometallic product, isolated in 52% yield as dark red microcrystals (eq 7). The bidentate coordination of the dmpe ligand was clearly established by NMR spectroscopy. The methyl protons of the $C_5Me_5$ ligand appear as a triplet ($\delta$ 1.86 ($J_{HP}$ = 1.0 Hz)) in the $^1H$ NMR spectrum; the methyl protons of the dmpe ligand appear as two virtual triplets ($\delta$ 0.67 ($^2J_{HP} + {}^5J_{HP}$ = 8.7 Hz), 0.75 ($^2J_{HP} + {}^5J_{HP}$ = 9.7 Hz)). In the $^{13}C\{^1H\}$ spectrum, the dmpe carbons appear as three virtual triplets. The dmpe phosphorus atoms appear as a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The IR spectrum of **8** displays a strong absorbance at 1386 cm$^{-1}$ indicative of a bent conformation for the nitrosyl ligand.[15]



(7)

**2** **8**

**Kinetics and Mechanism of the Reductive Elimination Reaction.** The rate of thermolysis of diphenylruthenium complex **2** with $PPh_3$ in benzene to product nitrosyl phosphine complex **6a** was followed by $^1H$ NMR spectroscopy; measured rate constants are given in Table II. The amount of **2** was quantified by $^1H$ NMR integration vs. ferrocene internal standard. The reaction is cleanly first order in **2** and shows no dependence on the concentration of phosphine. Measurement of the rate at five temperatures between 15 and 55 °C yielded the following activation parameters: $E_a$ = 22.5 ± 0.3 kcal/mol, $\Delta H^{\ddagger}$ = 21.9 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = −7 ± 2 cal/(deg·mol) (Figure 3). The rate was also determined for the reaction of **2** with $CH_2Cl_2$ and $PMe_3$ to give **5** and **6b**, respectively. Within experimental error, all the measured rates were found to be identical at 45 °C (Table II). This indicates strongly that these reactions proceed through the same rate-determining step.

Table II. First-Order Rate Constants for ($\eta^5$-$C_5Me_5$)Ru(NO)$Ph_2$ + L in $C_6D_6$

| $10^2$-[($\eta^5$-$C_5Me_5$)-Ru(NO)$Ph_2$], M | L | [L], M | temp, °C | $k_{obsd}$,[a] s$^{-1}$ |
|---|---|---|---|---|
| 1.72 | $PPh_3$ | 0.166 | 15 | 5.0 × $10^{-6}$ |
| 1.84 | $PPh_3$ | 0.168 | 25 | 2.0 × $10^{-5}$ |
| 2.03 | $PPh_3$ | 0.159 | 35 | 6.8 × $10^{-5}$ |
| 1.86 | $PPh_3$ | 0.165 | 45 | 2.1 × $10^{-4}$ |
| 1.86 | $PPh_3$ | 0.168 | 55 | 6.0 × $10^{-4}$ |
| 4.17 | $PPh_3$ | 0.181 | 45 | 2.3 × $10^{-4}$ |
| 1.87 | $PPh_3$ | 0.112 | 45 | 2.1 × $10^{-4}$ |
| 1.87 | $PPh_3$ | 0.250 | 45 | 2.2 × $10^{-4}$ |
| 1.88 | $PPh_3$ | 0.345 | 45 | 2.1 × $10^{-4}$ |
| 1.98 | $PMe_3$ | 0.104 | 45 | 1.9 × $10^{-4}$ |
| 1.95 | $CH_2Cl_2$ | 0.275 | 45 | 1.9 × $10^{-4}$ |
| 3.81 | $CH_2Cl_2$ | 0.245 | 45 | 2.0 × $10^{-4}$ |

[a] All values ±10%.

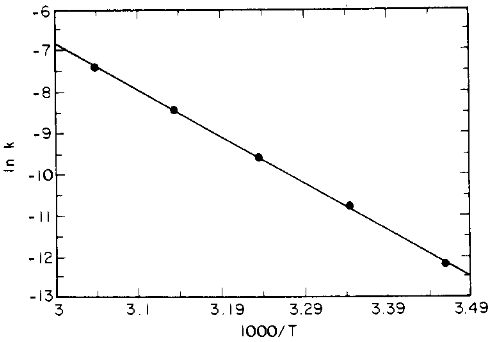
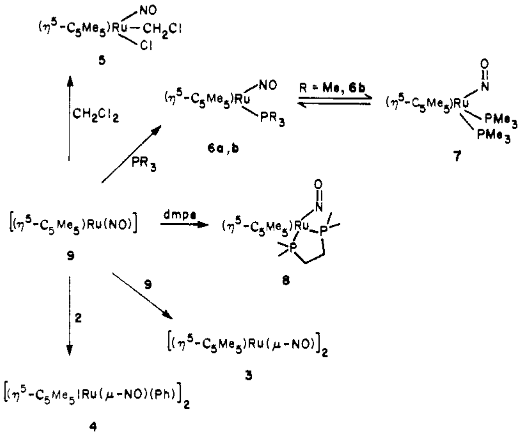


Figure 3. Arrhenius plot of the thermolysis of **2** + $PPh_3$ in $C_6D_6$ over the temperature range 15–55 °C.

Scheme I



The simplest mechanism consistent with the data involves initial rate-determining reductive elimination of biphenyl from **2**. This generates ($\eta^5$-$C_5Me_5$)Ru(NO) (**9**) or a solvated form of this species; this intermediate subsequently reacts to form the observed products (Scheme I). Intermediate **9** can be trapped by reaction

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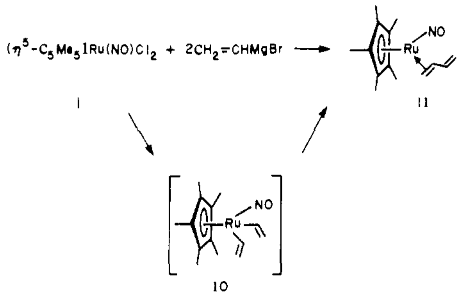
(14) A variety of ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$X (X = halide, hydride, and alkyl) derivatives are known: Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278.

(15) Linear NO IR stretching frequencies generally occur in the range 1600–1820 cm$^{-1}$: Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

Scheme II



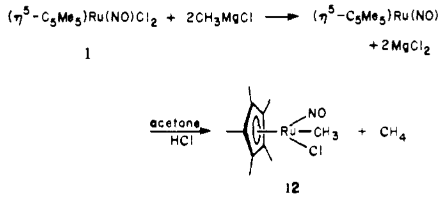
with a phosphine ligand or by insertion of the metal center into a C–Cl bond of $CH_2Cl_2$. We presume that nitrosyl dimer **3** forms by dimerization of intermediate **9**; diphenyl dimer **4** may arise by insertion of **9** into the ruthenium–phenyl bond of **2**, which is consistent with the increased amount of **4** produced with larger concentration of **2**. The different ratios of **3** to **4** observed in different solvents most likely depends on the ability of the solvent to stabilize intermediate **9**; larger amounts of dimer **3** are formed in more strongly coordinating media.

**Synthesis and Thermolysis Reactions of Analogues of Diphenyl Complex 2 Having sp$^2$- and sp$^3$-Hybridized Carbon Atoms Bound to Ruthenium.** In order to understand more clearly the causes of the difference in chemistry between diphenyl complex **2** and the related dialkyl complexes,[9] we decided to attempt the synthesis and study of analogous compounds having sp$^2$- and both sp$^2$- and sp$^3$-hybridized carbon atoms bound to ruthenium. Our first target was the divinyl analogue $(\eta^5\text{-}C_5Me_5)Ru(NO)(CH{=}CH_2)_2$ (**10**). Treatment of dichloride **1** with 2 equiv of $CH_2{=}CHMgBr$ yielded a product which was extracted from the crude reaction mixture with pentane to give a pure yellow oil, **11**, in ca. 60% yield (based on Ru). Compound **11** was characterized by $^1H$ and $^{13}C$ NMR spectroscopy, IR spectroscopy, and high-resolution mass spectrometry. NMR analysis of the pure product or the crude reaction mixture was not consistent with its formulation as a divinyl complex. The $^1H$ NMR spectrum displays two distinct sets of olefinic protons: one in a region typical for uncoordinated alkenes ($\delta$ 4.76 (dd, $J$ = 2.0, 9.8 Hz), 5.24 (dd, $J$ = 2.0, 16.4 Hz), 5.96 (m)), and the other significantly upfield ($\delta$ 2.08 (dd, $J$ = 2.6, 8.4 Hz), 2.82 (dd, $J$ = 2.6, 11.8 Hz), 3.21 (m)); a similar trend is also observed in the $^{13}C$ NMR spectrum. On the basis of these data, we assign the 18-electron $\eta^2$-butadiene structure $(\eta^5\text{-}C_5Me_5)Ru(NO)[\eta^2\text{-}(CH_2{=}CHCH{=}CH_2)]$, having a linear NO group, to **11**.[16]

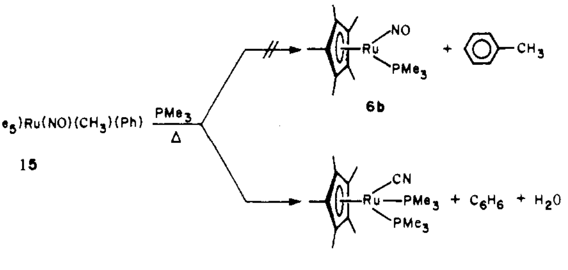
The stereochemical rigidity of the butadiene ligand at ambient temperature is clearly indicated by the sharp signals observed for the butadiene protons and carbons in the room-temperature $^1H$ and $^{13}C$ NMR spectra. Due to its instability at elevated temperatures, **11** could not be heated in order to observe an exchange process involving the butadiene ligand; fluxional behavior has been observed for other $\eta^2$-butadiene transition-metal complexes.[17] The butadiene ligand is presumably coordinated in a trans configuration; $J_{HH}$ for the internal protons (9.7 Hz) is similar to the corresponding $J_{HH}$ for free butadiene (which exists mainly in the trans configuration).[18] Compound **11** most likely arises from reductive elimination of butadiene from the very reactive transient divinyl species **10** (Scheme II).[19]

Our second synthetic target was an analogue of **2** having both an alkyl group and a sp$^2$-bound group. Accordingly, we decided to treat a ruthenium alkyl chloride derivative with the appropriate Grignard reagent. Unfortunately, attempts to monoalkylate dichloride compound **1** were unsuccessful. The best approach was found to be treatment of a dialkyl compound with a halogen acid to replace an alkyl group with a halide.[20] Thus, dichloride **1** was treated with $CH_3MgCl$ to generate $(\eta^5\text{-}C_5Me_5)Ru(NO)(CH_3)_2$. After excess Grignard reagent was removed by filtration through silica gel, the crude product was treated with an excess of aqueous HCl in acetone. Chloromethylruthenium compound **12** was isolated by crystallization in 60–70% yield as an air-stable, brown-red solid (Scheme III).

Scheme III

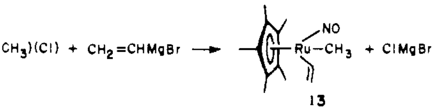


Scheme IV



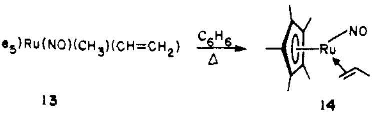
Interestingly, even under these relatively stringent conditions no dichloride **1** was regenerated; the metal–carbon bond in **12** is apparently unusually stable toward protonolysis. The assigned structure of **12** is fully supported by spectroscopic data and combustion analysis (see Experimental Section).

As expected, reaction of methyl chloride **12** with $CH_2{=}CHMgBr$ gave the new compound $(\eta^5\text{-}C_5Me_5)Ru(NO)(CH_3)(CH{=}CH_2)$ (**13**) (eq 8), a red solid which can be purified by sublimation at 40–50 °C at $10^{-4}$ torr in ca. 60% yield. The assignment of **13** is supported by spectroscopic and combustion analysis. The vinyl protons appear in the $^1H$ NMR spectrum as the expected ABC spin pattern.



(8)

Like the corresponding dimethyl and diethyl complexes, methylvinylruthenium compound **13** is stable in solution to ca. 100 °C. The products of thermolysis are, however, quite different. Compound **13** decomposes at 100 °C to give dimer **3** and a new product identified as the $\eta^2$-propene complex $(\eta^5\text{-}C_5Me_5)Ru(NO)[\eta^2\text{-}(CH_2{=}CHCH_3)]$ (**14**) (67% by $^1H$ NMR) (eq 9).



(9)

Following chromatography on silica gel, **14** was isolated as an air-sensitive, viscous yellow oil in 29% yield. Propene complex **14** was characterized by $^1H$ and $^{13}C$ NMR spectroscopy, IR spectroscopy, and high-resolution mass spectrometry. In the $^1H$ NMR spectrum, the propene protons appear as a first-order $A_3XYZ$ spin pattern. The $\beta$-proton appears as a doublet of doublets of quartets ($\delta$ 2.67 (1 H, $J$ = 6.2, 8.6, 12.0 Hz)). This reaction is an unusual example of a C–C reductive elimination that gives an isolable initially formed $\eta^2$-alkene complex.[21] This

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[16] A related ruthenium $\eta^2$-butadiene complex, $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)(\eta^2\text{-butadiene})]^+PF_6^-$, has been reported: Bruce, M. I.; Wong, F. S. *J. Organomet. Chem.* **1981**, *210*, C5–C8.

[17] Benn, R.; Jolly, P. W.; Joswig, T.; Mynott, R.; Schick, K.-P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 680–691 and references therein.

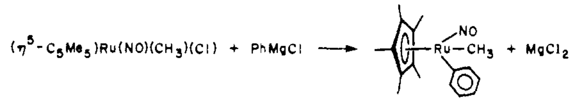
[18] Hubgood, R. T.; Goldstein, J. H. *J. Mol. Spectrosc.* **1964**, *12*, 76–86.

[19] (a) Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945–947. (b) An outer-sphere redox mechanism is also possible: Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1986**, *317*, 23–31 and references therein.

[20] (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1557–1562. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550.

lends credence to the idea that a similar process occurs to give $\eta^2$-butadiene complex **11**.

In analogy with the synthesis of **13**, treatment of methyl chloride complex **12** with PhMgCl produced the phenylmethylruthenium complex **15**, isolated in 37% yield (eq 10). Thermolysis of **15** at 130 °C led to multiple products, but no toluene was ever observed. However, heating **15** at 130 °C in the presence of an excess of $PMe_3$ led to the formation of the cyano bis(phosphine) complex $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CN$ (the same product formed in the thermolysis of the dimethyl analogue $(\eta^5\text{-}C_5Me_5)Ru(NO)(CH_3)_2$), presumably by a methyl-to-NO migratory insertion process (Scheme IV).[9]



(10)

12 15

**Relationship of Ligand Character and Reductive Elimination Propensity.** The thermal chemistry displayed by diphenyl complex **2**, methyl vinyl complex **13**, phenyl methyl complex **15**, and the (presumed) divinyl complex **10** indicates that in this system the vinyl ligand has a greater propensity to reductively eliminate than the phenyl ligand, and both participate in reductive elimination more readily than alkyl ligands. This trend is emphasized by the greater thermal stability of the dialkyl complexes and the lack of products resulting from reductive elimination. This supports the postulate[21,22] that $\pi$-coordination of the electrons in an eliminating ligand may stabilize the reductive elimination transition state.

Without knowledge of relative metal–carbon bond strengths in this system, it is difficult to ascertain whether these relative reductive elimination propensities are influenced primarily by (a) thermodynamic or (b) kinetic factors. With respect to the thermodynamic explanation, reductive elimination results in loss of two metal–carbon bonds and formation of one new carbon–carbon bond. If the C–C bond in the organic elimination product were unusually strong compared to the metal–carbon bonds in the rapidly reacting complexes, and this difference increased in going from the $sp^3$- to the $sp^2$-bonded systems, the difference might be felt partially in the transition state for elimination, resulting in a stabilization of this state and an increase in rate. The alternative kinetic explanation is the one suggested earlier for the rapidity of a related cobalt reductive elimination: that the rate is accelerated by partial coordination of the $\pi$-electrons of the eliminating group to the metal center in the elimination transition state.[22]

Some guesses can be made about explanation (a) based on thermodynamic information available for organic molecules and related organometallic systems. The C–C bond dissociation energy in ethane is 90 kcal/mol, and those in biphenyl and butadiene are 114 and 115 kcal/mol, respectively.[23] This suggests there might be a strong driving force for elimination of the $sp^2$-bonded organic molecules. However, there is evidence that the metal–$sp^2$ bonds are correspondingly strong. For example, recent calorimetric studies on $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(R)(H)$ reveal that the iridium–phenyl bond dissociation energy in this system is very high, lying 30 kcal/mol above those for corresponding iridium–alkyl bonds.[24] A similar trend is noted in the $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(R)(H)$ system, although the difference seems to be smaller in magnitude (Rh–Ph is 13 kcal/mol stronger than Rh–$CH_3$).[25] This bond dissociation energy difference between metal–phenyl and metal–alkyl bonds has been observed for several other systems.[26] It is not clear what energy values provide the best model for our ruthenium system, but to the extent that M–C and C–C bond dissociation energies both increase comparably as the amount of s character in the bond increases, the differential driving force for elimination becomes smaller.

Perhaps the most compelling argument in favor of the kinetic rather than the thermodynamic explanation for our relative rates comes from a comparison of the phenyl and vinyl systems. On the basis of the bond energies summarized above and with the assumption that the metal–vinyl bond dissociation energies are not substantially lower than those for metal–phenyl bonds, the driving force in the phenyl elimination reactions should be greater than those in the vinyl. However, the opposite seems to be the case. We believe this is more consistent with the $\pi$-coordination explanation, as the $\pi$-electrons of a vinyl group will undoubtedly coordinate more readily to the metal center than those in a benzene ring. Resolution of this problem will require the availability of accurate bond dissociation energy information for these ruthenium systems.

## Experimental Section

**General Remarks.** All manipulations were conducted under nitrogen or argon by using standard drybox, Schlenk, or vacuum line techniques, unless otherwise indicated. Experiments conducted in the drybox utilized a prescrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train and equipped with a −40 °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. $^1H$ NMR spectra were obtained at ambient temperature on either a Bruker AM500 or a 300-MHz instrument assembled by Mr. Rudi Nunlist at the University of California, Berkeley (UCB), NMR facility. Chemical shifts are reported in units of parts per million (ppm) ($\delta$) downfield from tetramethylsilane ($Me_4Si$). $^1H$ NMR shifts are relative to residual protiated solvent: benzene-$d_5$, $\delta$ 7.15; $CDHCl_2$, $\delta$ 5.32. $^{13}C$ NMR spectra were recorded at 75.5 MHz, and chemical shifts are reported relative to the solvent resonance: benzene-$d_6$, $\delta$ 128.00; $CD_2Cl_2$, $\delta$ 53.80. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz, and chemical shifts are given relative to external 85% $H_3PO_4$. All coupling constants are reported in hertz. "Virtual triplets" refer to non-first-order multiplets that resemble filled doublets; 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-6-4 $^3/_8$–$^1/_4$ 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 by using either silica gel (230–400 mesh ASTM, EM Reagents) or neutral alumina (activity III, 6% $H_2O$, Alfa).

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, diethyl ether ($Et_2O$), and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Ethanol 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. Trimethylphosphine ($PMe_3$) was purchased from Strem, dried over 1:5 Na:K alloy, and utilized exclusively

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[21] A similar reductive coupling to give a spectroscopically observed ($\eta^2$-olefin)palladium complex has been reported: Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174–4181.

[22] (a) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003–7011. (b) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101.

[23] Calculated from the heats of formation of the appropriate compounds and radicals: (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

[24] Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. S. *J. Am. Chem. Soc.*, in press.

[25] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

[26] (a) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280. (b) Bruno, J. W.; Marks, T. J.; Morss, L. R. *Ibid.* **1983**, *105*, 6824–6832. (c) Pilcher, G.; Skinner, H. A. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. P., Patai, S., Eds.; Wiley-Interscience: New York, 1982; Vol. 1, 43–90. (d) Yoneda, G.; Blake, D. M. *J. Organomet. Chem.* **1980**, *190*, C71–C74. (e) Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67–71.

by vacuum transfer. Triphenylphosphine ($PPh_3$) was purchased from Strem and recrystallized from hexane; 1,2-bis(dimethylphosphino)ethane (dmpe) was purchased from Strem and used as received. $(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2$ (**1**) was prepared following the method of Seidler and Bergman.[9]

**$(\eta^5\text{-}C_5Me_5)Ru(NO)Ph_2$ (2).** A 100-mL round-bottom flask equipped with a magnetic stir bar was loaded with 0.375 g (1.11 mmol) of $(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2$ (**1**) and 30 mL of 1:1 v/v THF/hexane. To this stirring green slurry was slowly added 1.20 mL (2.40 mmol) of a THF solution of PhMgCl dropwise via syringe. Addition of the PhMgCl caused the reaction mixture to quickly turn dark red in color. The mixture was stirred for 2 h and then filtered through silica gel and the silica washed with $Et_2O$ (ca. 30 mL) until the filtrates were colorless. The combined filtrates were cooled to −40 °C to give 0.251 g (54%) of dark red block-like crystals of **2**. The mother liquors were concentrated under vacuum, and the residue was purified by crystallization from toluene layered with an equal portion of pentane to give a total yield of 0.348 g (75%): mp 109 °C dec; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.74 (s, 15 H), 6.93 (m, 2 H), 7.03 (m, 4 H), 7.22 (m, 4 H); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 9.84 ($C_5\mathit{Me}_5$), 106.51 ($\mathit{C}_5Me_5$), 123.20 (para), 127.85 (meta), 138.99 (ortho), 157.90 (ipso); MS (EI), *m/e* 419 ($M^+ - 2$), 155 (base). Anal. Calcd for $C_{22}H_{25}NORu$: C, 62.84; H, 5.99; N, 3.33. Found: C, 63.06; H, 5.91; N, 3.28.

**Thermolysis of 2 in Benzene, $CH_3CH_2OH$, $CH_3CN$, or Hexane.** A 50-mL glass bomb was loaded with 53.7 mg (0.128 mmol) of **2** and 7 mL of benzene. The reaction mixture was degassed by three freeze–pump–thaw cycles on the vacuum line and heated under vacuum for 24 h at 45 °C. Following concentration under vacuum, the dark brown residue was separated by column chromatography in the drybox on silica gel (2 × 10 cm). Biphenyl was eluted with hexane. A dark purple band was eluted with 3:1 hexane/$Et_2O$ followed by a red band of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)]_2$ (**3**) (vide infra). The purple fraction was concentrated under vacuum and the residue crystallized from pentane at −40 °C to give 15.3 mg (35% based on Ru) of phenyl dimer **4**: mp 181–182 °C dec; IR (benzene-$d_6$) 1654 (m), 1559 (m), 1541 (m), 1506 (m), 1497 (s), 1474 (m), 1457 (m), 727 (m) $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.56 (s, 30 H), 6.36 (m, 10 H); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 9.30 ($C_5\mathit{Me}_5$), 102.99 ($\mathit{C}_5Me_5$), 121.76 (para), 125.96 (meta), 133.81 (ortho), 152.93 (ipso); MS (EI), *m/e* 687 ($M^+$), 314 (base). Anal. Calcd for $C_{32}H_{40}N_2O_2Ru_2$: C, 55.96; H, 5.87; N, 4.08. Found: C, 56.12; H, 5.88; N, 4.12. The product ratio of **3**:**4** as a function of the concentration of **2** was determined by loading NMR tubes with benzene-$d_6$ solutions of varying concentrations of **2**, connecting the tubes to Cajon adapters, degassing the tubes with three freeze–pump–thaw cycles, and flame-sealing under vacuum. The tubes were then heated at 45 °C for 40 h. Amounts of starting material and products were quantified by using $^1H$ NMR spectroscopy by integration of the $C_5Me_5$ proton resonances vs. an internal standard of ferrocene (see experimental description of $^1H$ NMR spectroscopy kinetics).

Similarly, a 20-mL glass bomb was loaded with 55.4 mg (0.132 mmol) of **2** and 5 mL of $CH_3CH_2OH$ was added by vacuum transfer. The bomb was heated at 45 °C under vacuum for 48 h and concentrated under vacuum, and the contents were transferred to a sublimation apparatus. Biphenyl (8.30 mg, 41% yield) was sublimed at $10^{-4}$ torr at ambient temperature leaving behind 34.8 mg (99%) of pure dimer **3**. A 20-mL glass bomb loaded with 51.7 mg of **2** and 5 mL of $CH_3CN$ was heated at 45 °C under vacuum for 48 h. Biphenyl (10.8 mg, 57% yield) and dimer **3** (31.9 mg, 98% yield) were separated by sublimation as previously. In both the $CH_3CH_2OH$ and $CH_3CN$ experiments, $^1H$ NMR analysis of the crude reaction mixture showed dimer **3** as the sole organometallic product. Thermolysis of **2** (0.118 g, 0.281 mmol) in hexane (7 mL) at 45 °C under vacuum in a 50-mL bomb produced dimer **4** as the main organometallic product (87% by $^1H$ NMR integration). Compound **4** was isolated by column chromatography in air on silica gel (2 × 7 cm) by elution with benzene. Subsequent crystallization of the fraction from pentane at −40 °C gave 43.0 mg (45%) of 4.

**Independent Synthesis of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)]_2$ (3).** A 50-mL round-bottom flask with an attached vacuum stopcock side arm was loaded with 0.100 g (0.297 mmol) of $(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2$ (**1**) and 0.495 g (7.57 mmol) of zinc powder and equipped with a magnetic stir bar and a serum septum. The reaction flask was placed under a positive pressure of nitrogen on the Schlenk line, purged, and charged with 20 mL of deaerated absolute ethanol via syringe. The reaction mixture was stirred for 40 min, concentrated under vacuum, and then brought into the drybox. The residue was redissolved in $Et_2O$ and filtered through a plug of 5% Norite/Celite. The plug was washed with $Et_2O$ until the filtrate was colorless and the solvent removed from the combined filtrates in vacuo to give 57.6 mg (73%) of red powder **4**: mp, no detectable melting point or decomposition below 240 °C; IR (KBr) 2960 (m), 2915 (m), 1735 (m), 1535 (s), 1465 (m), 1455 (m), 1385 (s), 1025 (m), 700 (s), 615 (m) $cm^{-1}$; $^1H$ NMR (benzene-$d_6$) $\delta$ 1.47 (s); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 8.41 ($C_5\mathit{Me}_5$), 97.11 ($\mathit{C}_5Me_5$); MS (EI), *m/e* 534 ($M^+ + 1$), 78 (base). Anal. Calcd for $C_{20}H_{30}N_2O_2Ru_2$: C, 45.10; H, 5.68; N, 5.26. Found: C, 45.18; H, 5.63; N, 4.89.

**Thermolysis of 2 with $CH_2Cl_2$.** A 50-mL glass bomb loaded with 80.0 mg of **2** was charged with 20 mL of $CH_2Cl_2$ by vacuum transfer. The mixture was heated for 48 h at 45 °C under vacuum. During this time period the solution changed color from dark red to brown. The reaction mixture was cooled to ambient temperature and concentrated under vacuum. Biphenyl was removed by sublimation into a trap held at −196 °C. The dark brown residue was partially purified by column chromatography on silica gel. Elution with 1:1 hexane/toluene removed a dark brown band of **5** which was concentrated under vacuum. $^1H$ NMR analysis estimated the purity to be ca. 90%; a total of 30.0 mg (41% based on Ru) was collected. Further attempts to purify **5** were unsuccessful. Partial characterization of **5**: $^1H$ NMR (benzene-$d_6$) $\delta$ 1.32 (s, 15 H), 3.88 (d, 1 H, $J = 7.2$ Hz), 5.94 (d, 1 H, $J = 7.2$ Hz); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 8.82 ($C_5\mathit{Me}_5$), 43.44 ($\mathit{C}H_2Cl$), 108.08 ($\mathit{C}_5Me_5$); MS (EI), *m/e* 351 ($M^+$), 302 (base).

**Thermolysis of 2 with $PR_3$ (R = Ph, Me).** A 15-mL glass bomb charged with 68.5 mg (0.163 mmol) of **2**, 130 mg (0.496 mmol) of $PPh_3$, and 4 mL of benzene was degassed with three freeze–pump–thaw cycles on the vacuum line and heated under vacuum at 45 °C for 48 h. The benzene was removed under vacuum leaving a dark brown oil. The residue was washed with hexane and then separated by column chromatography on silica gel. A yellow fraction was eluted with benzene and concentrated under vacuum. The fraction was purified by crystallization from toluene layered with an equal portion of hexane at −40 °C to give 17.6 mg (20%) of dark yellow flakes of **6a**: mp 164–166 °C; $^1H$ NMR (benzene-$d_6$) $\delta$ 1.74 (d, 15 H, $J_{HP} = 1.0$ Hz), 7.05 (m, 9 H), 7.77 (m, 6 H); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 10.97 ($C_5\mathit{Me}_5$), 94.03 ($\mathit{C}_5Me_5$), 128.16 (meta, d, $J_{CP} = 9.9$ Hz), 129.77 (para), 134.58 (ortho, d, $J_{CP} = 12.6$ Hz), 135.71 (ipso, d, $J_{CP} = 21.7$ Hz); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 64.48; MS (EI), *m/e* 529 ($M^+$), 277 (base). Anal. Calcd for $C_{28}H_{30}NOPRu$: C, 63.62; H, 5.72; N, 2.65; P, 5.86. Found: C, 63.80; H, 5.58; N, 2.73; P, 5.46.

In a similar manner, **2** (77.7 mg, 0.185 mmol) was heated in the presence of $PMe_3$ (3.94 mmol, added by vacuum transfer) in 3 mL of benzene under vacuum in a 10-mL glass bomb for 24 h at 45 °C. The mixture was concentrated under vacuum, biphenyl removed by sublimation, and the residue purified by crystallization from pentane at −40 °C to give 23.0 mg (36%) of dark red crystals of **6b**: mp 157–160 °C; $^1H$ NMR (benzene-$d_6$) $\delta$ 1.15 (d, 9 H, $J_{HP} = 8.9$ Hz), 1.92 (d, 15 H, $J_{HP} = 1.0$ Hz); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 11.71 ($C_5\mathit{Me}_5$), 19.21 ($P\mathit{Me}_3$, d, $J_{CP} = 28.7$ Hz), 92.58 ($\mathit{C}_5Me_5$); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ −1.74; MS (EI), *m/e* 343 ($M^+ + 1$), 77 (base). Anal. Calcd for $C_{13}H_{24}NOPRu$: C, 45.64; H, 7.07; N, 4.09. Found: C, 45.82; H, 7.15; N, 3.94.

**Generation of $(\eta^5\text{-}C_5Me_5)Ru(NO)(PMe_3)_2$ (7).** A NMR tube was loaded with 19.0 mg (0.0555 mmol) of **6b** and 0.7 mL of benzene-$d_6$ and connected to a Cajon adapter. The tube was degassed with three freeze–pump–thaw cycles on the vacuum line and 0.463 mmol of $PMe_3$ added by vacuum transfer. The tube was flame-sealed under vacuum and brought to ambient temperature; spectroscopic data for **7**: $^1H$ NMR (benzene-$d_6$) $\delta$ 1.76 (t, 15 H, $J_{HP} = 1.0$ Hz), 0.87 (vt, 18 H, $^2J_{HP} + {}^5J_{HP} = 8.2$ Hz); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 11.34 ($C_5\mathit{Me}_5$), 19.37 ($P\mathit{Me}_3$, vt, $^1J_{CP} + {}^3J_{CP} = 27.4$ Hz), 102.85 ($\mathit{C}_5Me_5$); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 8.97.

**Thermolysis of 2 with 1,2-Bis(dimethylphosphino)ethane.** A 10-mL glass bomb was charged with 74.2 mg (0.176 mmol) of **2**, 0.247 g (1.64 mmol) of 1,2-bis(dimethylphosphino)ethane (dmpe), and 3 mL of benzene. The bomb was degassed with three freeze–pump–thaw cycles and heated for 20 h at 45 °C. The volatile materials were removed in vacuo, and the residue was purified by crystallization from toluene layered with an equal portion of pentane at −40 °C to yield 38.0 mg (52%) of dark red microcrystals of **8**: mp 137–139 °C; $^1H$ NMR (benzene-$d_6$) $\delta$ 0.66 (vt, 6 H, $^2J_{HP} + {}^5J_{HP} = 8.7$ Hz), 0.75 (vt, 6 H, $^2J_{HP} + {}^5J_{HP} = 9.7$ Hz), 0.87 (m, 2 H), 1.87 (t, 15 H, $J_{HP} = 1.0$ Hz, m, 2 H (overlap)); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 11.36 ($C_5\mathit{Me}_5$), 13.23 ($P\text{–}\mathit{C}H_3$, vt, $^1J_{CP} + {}^4J_{CP} = 25.6$ Hz), 17.70 ($P\text{–}\mathit{C}H_3$, vt, $^1J_{CP} + {}^4J_{CP} = 23.8$ Hz), 29.01 ($P\text{–}\mathit{C}H_2\mathit{C}H_2\text{–}P$, vt, $^1J_{CP} + {}^2J_{CP} = 48.4$ Hz), 102.91 ($\mathit{C}_5Me_5$); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 55.53; MS (EI), *m/e* 417 ($M^+ + 1$), 387 (base). Anal. Calcd for $C_{16}H_{31}NOP_2Ru$: C, 46.15; H, 7.50; N, 3.36. Found: C, 45.92; H, 7.54; N, 3.20.

**Kinetics of the Thermolysis of 2 in Benzene-$d_6$ by $^1H$ NMR Spectroscopy.** Samples were prepared by flame-sealing under vacuum 5-mm NMR tubes loaded with the appropriate reagents, heated in a factory calibrated Neslab Endocal Model RTE-8DD constant temperature bath filled with distilled water, and frozen rapidly in ice water after removal from the bath. Typically, the reactions were monitored to greater than 3 half-lives by ambient-temperature $^1H$ NMR spectroscopy by integrating the $C_5Me_5$ proton resonances of **2** 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 2 min. All kinetic plots displayed excellent linearity with correlation coefficients of 0.998 or better.

**Reaction of $(\eta^5\text{-}C_5Me_5)Ru(NO)Cl_2$ (1) with $CH_2{=}CHMgBr$.** A stirring mixture of 96.2 mg (0.285 mmol) of **1** in 20 mL of 1:1 v/v THF/hexane in a 50-mL round-bottom flask was treated with 0.600 mL (0.600 mmol) of a THF solution of $CH_2{=}CHMgBr$ by dropwise addition *via* syringe. The green solution turned golden upon addition of the Grignard reagent. The mixture was stirred for 2 h and then concentrated under vacuum. The residue was extracted with ca. 30 mL of pentane, and the extracts were filtered through a plug of glass wool. Concentration of the extracts under vacuum left 57.2 mg (63%) of **11** as a golden oil: $^1$H NMR (benzene-$d_6$) $\delta$ 1.55 (s, 15 H), 2.08 (dd, 1 H, $J$ = 2.6, 8.4 Hz), 2.82 (dd, 1 H, $J$ = 2.6, 11.8 Hz), 3.21 (m, 1 H), 4.76 (dd, 1 H, $J$ = 2.0, 9.8 Hz), 5.24 (dd, 1 H, $J$ = 2.0, 16.4 Hz), 5.96 (m, 1 H); $^{13}$C NMR (benzene-$d_6$) $\delta$ 10.07 ($C_5\mathit{Me}_5$, q, $J$ = 127.2 Hz), 37.15 ($=\mathit{C}H_2$, coordinated, t, $J$ = 155.2 Hz), 60.07 ($=\mathit{C}H$, coordinated, d, $J$ = 150.1), 97.72 ($\mathit{C}_5Me_5$), 107.28 ($=\mathit{C}H_2$, free, t, $J$ = 158.2 Hz), 145.47 ($=\mathit{C}H$, free, d, $J$ = 152.7 Hz); high resolution MS (EI), *m/e* calcd for $^{12}C_{14}{}^{1}H_{21}{}^{14}N^{16}ORu$ 323.0677/321.0665 ($M^+$, $^{104}$Ru/$^{102}$Ru), 293.0697/291.0685 ($M^+$ – NO, $^{104}$Ru/$^{102}$Ru), *m/e* found 323.0661/321.0672 ($M^+$, $^{104}$Ru/$^{102}$Ru, deviation = –5.0/1.7 ppm), 293.0695/291.0673 ($M^+$ – NO, $^{104}$Ru/$^{102}$Ru, deviation = –0.9/–4.6 ppm).

**$(\eta^5\text{-}C_5Me_5)Ru(NO)(Me)(Cl)$ (12).** A 100-mL round-bottom flask equipped with a magnetic stir bar was charged with 0.306 g (0.906 mmol) of **1** and 40 mL of 3:1 v/v hexane/THF. To the stirring mixture was added via syringe 0.650 mL (1.82 mmol) of a THF solution of MeMgCl. The green slurry turned a golden brown. After stirring for 1 h, the solution was filtered through silica gel into a 100 mL Schlenk flask which was equipped with a magnetic stir bar. The silica was washed with hexane until the filtrate was colorless. After concentration under vacuum, the combined filtrates were placed under a nitrogen atmosphere on the Schlenk line and then dissolved in acetone (undried). To this stirring red solution was added 2.0 mL of 12 M HCL(aq) dropwise *via* syringe. This solution was allowed to stir for 12 h, and then the volatile components were removed under vacuum. The residue was purified by crystallization from 4:1 v/v pentane/toluene at –40 °C to give 0.219 g (76%) of brown crystals of **12**: mp 145–147 °C dec; $^1$H NMR (benzene-$d_6$) $\delta$ 1.25 (s, 15 H), 1.64 (s, 3 H); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 4.15 (*Me*), 9.08 ($C_5\mathit{Me}_5$), 106.19 ($\mathit{C}_5Me_5$); MS (EI), *m/e* 317 ($M^+$), 234 (base). Anal. Calcd for $C_{11}H_{18}ClNORu$: C, 41.71; H, 5.73; N, 4.42. Found: C, 41.55; H, 5.73; N, 4.33.

**$(\eta^5\text{-}C_5Me_5)Ru(NO)(Me)(CH{=}CH_2)$ (13).** A 25-mL round-bottom flask equipped with a magnetic stir bar was loaded with 66.1 mg (0.209 mmol) of **12** and 10 mL of 3:1 v/v hexane/THF. To the reddish brown stirring mixture was added 0.22 mL (0.22 mmol) of a THF solution of $CH_2{=}CHMgBr$ via syringe which caused a color change to deep red. After being stirred for 3 h, the reaction mixture was filtered through neutral alumina (III), and the alumina washed with hexane until the filtrate was colorless. The combined filtrates were concentrated in vacuo, and the residue was purified by sublimation at 30–40 °C and $10^{-4}$ torr to give 37.7 mg (60%) of dark red solid **13**: mp 33–34 °C; $^1$H NMR (benzene-$d_6$) $\delta$ 0.90 (s, 3 H), 1.40 (s, 15 H), 5.64 (dd, 1 H, $J$ = 1.46, 16.8 Hz), 6.20 (dd, 1 H, $J$ = 1.44, 9.3 Hz), 7.19 (dd, 1 H, $J$ = 9.3, 16.9 Hz); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ –0.75 (*Me*, q, $J$ = 134.5 Hz), 9.63 ($C_5\mathit{Me}_5$, q, $J$ = 127.6 Hz), 103.22 ($\mathit{C}_5Me_5$), 120.36 ($-CH{=}\mathit{C}H_2$, t, $J$ = 153.6 Hz), 156.89 ($-\mathit{C}H{=}CH_2$, d, $J$ = 147.3 Hz); MS (EI), *m/e* 309 ($M^+$ + 1), 237 (base). Anal. Calcd for $C_{13}H_{21}NORu$: C, 50.63; H, 6.86; N, 4.54. Found: C, 50.56; H, 7.03; N, 4.86.

**Thermolysis of 13 in Benzene.** A 50-mL glass bomb was loaded with 53.0 mg (0.172 mmol) of **13** and 10 mL of benzene. The contents were degassed with three freeze–pump–thaw cycles on the vacuum line and heated under vacuum in an oil bath at 100 °C for 14 h. The solution was cooled to ambient temperature, and the volatile components were removed under vacuum. The residue was purified by column chromatography in the drybox on alumina (2 × 7 cm) eluting with 3:1 v/v hexane/$Et_2O$. A yellow band was eluted followed by a red band of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)]_2$ (**3**). The yellow band was concentrated under vacuum to give 15.4 mg (29%) of yellow oil **14**: $^1$H NMR ($CD_2Cl_2$) $\delta$ 1.60 (d, 3 H, $J$ = 6.2 Hz), 1.89 (s, 15 H), 2.03 (dd, 1 H, $J$ = 8.6, 1.7 Hz), 2.36 (dd, 1 H, $J$ = 12.1, 1.6 Hz), 2.67 (ddq, 1 H, $J$ = 6.2, 8.6, 12.0 Hz); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 10.49 ($C_5\mathit{Me}_5$), 23.37 ($\mathit{C}H_3$), 40.49 ($=\mathit{C}H_2$), 55.43 ($=\mathit{C}H$), 97.82 ($\mathit{C}_5Me_5$); high-resolution MS (EI), *m/e* calcd for $^{12}C_{13}{}^{1}H_{21}{}^{14}N^{16}ORu$ 311.0677/309.0666 ($M^+$, $^{104}$Ru/$^{102}$Ru), 267.0197/269.0208 ($M^+$ – $C_3H_6$, $^{104}$Ru/$^{102}$Ru), *m/e* found 311.0662/309.0664 ($M^+$, $^{104}$Ru/$^{102}$Ru, deviation = –4.7/–0.7 ppm), 269.0203/267.0191 ($M^+$ – $C_3H_6$, $^{104}$Ru/$^{102}$Ru, deviation = –1.5/–2.2 ppm).

**$(\eta^5\text{-}C_5Me_5)Ru(NO)(Me)(Ph)$ (15).** A 25-mL round-bottom flask was charged with 49.9 mg (0.158 mmol) of methylchlororuthenium complex **12** and 10 mL of 2:1 v/v hexane/THF and equipped with a magnetic stirbar. To the stirring mixture was added 0.08 mL (0.16 mmol) of a THF solution of PhMgCl dropwise via syringe. The brown solution turned reddish upon the addition of the Grignard reagent. The solution was stirred for 40 min and filtered through a plug of silica gel, and the filtrates were concentrated under vacuum. The residue was purified by crystallization from pentane to give 20.7 mg (37%) of dark red flakes of **15**: mp 173–175 °C; $^1$H NMR ($CD_2Cl_2$) $\delta$ 0.80 (s, 3 H), 1.69 (s, 15 H), 6.97 (m, 1 H), 7.06 (m, 2 H), 7.17 (m, 2 H); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 8.35 ($C_5\mathit{Me}_5$), 15.78 ($\mathit{C}H_3$), 96.95 ($\mathit{C}_5Me_5$) 113.92 (para), 117.62 (meta), 127.32 (ortho), 142.54 (ipso); MS (CI, $CH_4$), *m/e* 360 ($M^+$ + 2), 55 (base). Anal. Calcd for $C_{17}H_{23}NORu$: C, 56.96; H, 6.47; N, 3.91. Found: C, 57.09; H, 6.41; N, 3.86.

**Thermolysis of 15 with $PMe_3$.** An NMR tube was loaded with 6.0 mg (0.0167 mmol) of **15** and 0.7 mL of benzene-$d_6$ and connected to a Cajon adapter. The tube was degassed with three freeze–pump–thaw cycles on the vacuum line and 0.0605 mmol of $PMe_3$ added by vacuum transfer and flame-sealed under vacuum. The tube was then heated for 19 h at 130 °C. $^1$H and $^{31}P\{^1H\}$ NMR spectroscopy revealed the main $C_5Me_5$-containing product (70%) to be $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CN$: $^1$H NMR (benzene-$d_6$) $\delta$ 1.16 (vt, 18 H, $^2J_{HP} + {}^4J_{HP}$ = 8.4 Hz), 1.66 (t, 15 H, $J_{HP}$ = 1.4 Hz); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 7.2 [lit.[9] $^1$H NMR (benzene-$d_6$) $\delta$ 1.16 (vt, 18 H, $^2J_{HP} + {}^4J_{HP}$ = 8.4 Hz), 1.66 (t, 15 H, $J_{HP}$ = 1.4 Hz); $^{31}P\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 7.2].

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