were copyrolyzed as above. The products were isoprene, recovered VI, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, IIIc (15%), and IVc (8%).

IIIc is a liquid. It had the following spectral properties: $^1$H NMR $\delta$ 6.01–5.84 (m, CH═CH$_2$), 0.248–0.154 (m, CH$_3$); $^{13}$C NMR $\delta$ 136.13, 135.82, 133.65, 133.45, 133.36 (vinyl carbons), −0.976, −1.106 (methyl carbons); IR $\nu$ 1100, 1040 (SiO), 1600 cm$^{-1}$ (C═C); mass spectrum, *m/e* (relative intensities) 576 (30, M$^{+\cdot}$), 561 (100, M − 15$^+$), 549 (35), 449 (43), 437 (72). High-resolution mass spectrum of the M$^{+\cdot}$ ion: calcd for $C_{18}H_{36}Si_7O_8$, 576.0795; found, 576.0790. Anal. Calcd for $C_{18}H_{36}Si_7O_8$: C, 37.47; H, 6.29. Found: C, 37.44; H, 6.24.

IVc is a liquid which has the following spectral properties: $^1$H NMR $\delta$ 6.065–5.88 (m, CH═CH$_2$), 0.26–0.16 (m, CH$_3$); $^{13}$C NMR $\delta$ 135.78, 135.09, 134.60, 134.49, 134.23, 133.64, 133.46 (vinyl carbons), −0.96, −1.17, −1.44 (methyl carbons); IR $\nu$ 1100, 1040 cm$^{-1}$ (SiO), 1600 cm$^{-1}$ (C═C). Anal. Calcd for $C_{18}H_{36}Si_8O_{10}$: C, 33.93; H, 5.68. Found: C, 33.83; H, 5.38.

**Acknowledgment.** This work was supported in part by the Air Force Office of Scientific Research, No. 82-0333 and No. 86-0042.

**Registry No.** I, 63683-92-1; IIIa, 34060-11-2; IIIb, 103202-53-5; IIIc, 103202-56-8; IVa, 103202-51-3; IVb, 103202-54-6; IVc, 103202-57-9; V, 7418-20-4; VI, 103202-55-7; $D_3$, 541-05-9; $D_4$, 556-67-2; isoprene, 78-79-5; 2,2,5,5,9,9,13,13-octamethyl-2,5,7,9,12-pentasila-1,6,8,13-tetraoxaspiro[6.6]tridecane, 103202-52-4; hXaethylcyclotrisiloxane, 2031-79-0; octaethylcyclotetrasiloxane, 1451-99-6.

**Supplementary Material Available:** A listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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# Preparation and C–N Cleavage Reactions of Bis[(dimethylphosphino)ethane]ruthenium Isocyanide Complexes

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The thermal reaction of (DMPE)$_2$Ru(naphthyl)H [DMPE = bis(dimethylphosphino)ethane] with isocyanides is described. Thermolysis in the presence of excess neopentyl isocyanide at 60 °C in benzene solution results in the formation of the simple substitution complex (DMPE)$_2$Ru(CNCH$_2$CMe$_3$) plus naphthalene. Thermolysis in the presence of excess phenyl isocyanide results in the formation of the unusual monodentate DMPE complex Ru($\eta^2$-DMPE)($\eta^1$-DMPE)(CNPh)$_2$. Continued heating ultimately forms Ru(DMPE)$_2$(CNPh) plus phenyl isocyanide polymer. Thermolysis with ethyl isocyanide leads to the formation of Ru(DMPE)$_2$(CNEt). Thermolysis in the presence of *tert*-butyl isocyanide produces two organometallic products, Ru(DMPE)$_2$(CN)$_2$ and Ru(DMPE)$_2$(CN)H, plus four organic products, trimethylacetonitrile, naphthalene, isobutylene, and isobutane. A mechanism is suggested for the formation of these rearrangement and C–N bond cleavage products. The dicyanide molecule Ru(DMPE)$_2$(CN)$_2$ was found to crystallize in the orthorhombic space group *Pccn* with $a$ = 9.2842 (14) Å, $b$ = 14.1091 (30) Å, $c$ = 16.3641 (50) Å, $V$ = 2143.6 (1.4) Å$^3$, and $Z$ = 4.

## Introduction

Isocyanide complexes have been known for many years as isoelectronic analogues of carbon monoxide complexes. The chemistry of the coordinated isocyanide ligand, however, shows some distinct differences from that of CO with regard to reactions at both the metal–carbon linkage and the heteroatom. For example, the isocyanide ligand is generally believed to insert more readily into metal–alkyl bonds than is CO and often undergoes multiple insertions.[1] Isocyanides have also been observed to insert into the metal–hydrogen bond to generate formamyls.[2] More recently, isocyanide ligands have been observed to couple, forming new carbon–carbon bonds.[3]

The exclusive chemistry of the isocyanide ligand also extends to the chemistry of the C–N single bond. Isocyanide ligands can be formed by alkylation of a cyanide ligand.[4] Similarly, cyanide and hydride complexes have been formed by decomposition reactions of the coordinated isocyanide, usually in cationic complexes, although the true nature of these interconversions were never elucidated.[5]

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**Table I. $^1$H NMR Data ($\delta$) for Complexes in $C_6D_6$**

| compd | DMPE resonances[a] | other resonances |
|---|---|---|
| Ru(DMPE)$_2$(naphthyl)H (**1**) | 1.365 (d, $J$ = 5.4 Hz, 3 H), 1.208 (t, $J$ = 6.8 Hz, 6 H), 1.106 (t, $J$ = 8.8 Hz, 6 H), 0.987 (d, $J$ = 4.9 Hz, 3 H), 0.887 (t, $J$ = 10.7 Hz, 6 H) | 8.335 (dd, $J$ = 8.1, 3.2 Hz, 1 H), 8.243 (d, $J$ = 3.9 Hz, 1 H), 7.810 (d, $J$ = 8.3 Hz, 1 H), 7.761 (d, $J$ = 8.3 Hz, 1 H), 7.515 (d, $J$ = 8.3 Hz, 1 H), 7.378 (t, $J$ = 7.1 Hz, 1 H), 7.254 (t, $J$ = 7.8 Hz, 1 H), −8.547 (dq, $J$ = 90.8, 22.6 Hz, 1 H) |
| Ru(DMPE)$_2$(CNCH$_2$CMe$_3$) | 1.335 (br s, ~32 H) | 3.266 (s, 2 H), 1.084 (s, 9 H) |
| Ru($\eta^1$-DMPE)($\eta^2$-DMPE)(CNC$_6$H$_5$)$_2$ (**2**) | 1.366 (d, $J$ = 7.5 Hz, 6 H), 1.294 (d, $J$ = 7.6 Hz, 12 H), 0.785 (d, $J$ = 2.6 Hz, 6 H | 7.569 (d, $J$ = 7.5 Hz, 4 H), 7.195 (t, $J$ = 7.7 Hz, 4 H), 6.954 (t, $J$ = 7.3 Hz, 2 H) |
| Ru(DMPE)$_2$(CNC$_6$H$_5$) (**3**) | 1.267 (br s, ~32 H) | 7.687 (d, $J$ = 7.2 Hz, 2 H), 7.266 (t, $J$ = 7.8 Hz, 2 H), 6.974 (t, $J$ = 7.8 Hz, 1 H) |
| Ru(DMPE)$_2$(CNEt) | 1.323 (br s, ~35 H) | 3.425 (q, $J$ = 8 Hz, 2 H) |
| Ru(DMPE)$_2$(CN)H | | |
| *cis*-**4** | 1.895 (t, $J$ = 3.7 Hz), 1.733 (dd, $J$ = 6.9, 3.9 Hz), 1.507 (d, $J$ = 7.0 Hz), 0.8–1.3 (multiplets) | −9.28 (dq, $J$ = 83, 24 Hz, 1 H) |
| *trans*-**4** | 1.100 (br s, 24 H), 1.498 (br s, 8 H) | −12.75 (quint, $J$ = 22 Hz, 1 H) |
| Ru(DMPE)$_2$(CN)$_2$ (**5**)[b] | 1.741 (t, $J$ = 3.9 Hz, 6 H), 1.525 (t, $J$ = 2.7 Hz, 6 H), 1.488 (d, $J$ = 7.9 Hz, 6 H), 1.398 (d, $J$ = 6.8 Hz, 6 H) | |

[a] DMPE methylene resonances in *cis*-Ru(DMPE) XY complexes were not observed due to multiple H–H and P–H couplings. [b] Acetone-$d_6$ solvent.

We have recently reported the functionalization of activated carbon–hydrogen bonds with (C$_5$Me$_5$)Rh(CNR)$_2$.[6] Parallel to this examination, the insertion of isocyanide into the aromatic C–Ru bond in the well-known[7] oxidative addition adduct Ru(DMPE)$_2$(naphthyl)H was attempted. This paper describes a variety of these isocyanide complexes, and their rearrangement chemistry involving C–H and C–N bond cleavage reactions.

## Results

**A. Thermolysis of 1 with Neopentyl Isocyanide.** Upon heating a 0.15 M benzene-$d_6$ solution of Ru(DMPE)$_2$(naphthyl)H (**1**) at 60 °C for 18 h in the presence of 1.5 equiv of neopentyl isocyanide, a slow change in the $^1$H NMR spectrum is observed. In the aromatic region of the spectrum, two doublets of doublets attributable to free naphthalene are observed to appear at $\delta$ 7.618 and 7.241 ($J$ = 6.1, 3.3 Hz). The resonances of free neopentyl isocyanide ($\delta$ 0.587 (s, 9 H), 2.348 (t, $J$ = 1.7 Hz, 2 H)) were observed to decrease, while new resonances for coordinated isocyanide appeared at $\delta$ 1.078 (s, 9 H) and 3.257 (br s, 2 H). The coordinated DMPE resonances, initially a complicated overlapping series of doublets between $\delta$ 0.8 and 1.4 due to the eight different methylphosphine groups of **1**, appeared as a large broad singlet ($\nu_{1/2}$ = 8 Hz) at $\delta$ 1.330 (~32 H). Removal of solvent followed by sublimation in vacuo (75 °C) afforded the pure product. The IR spectrum shows a single strong low energy C=N stretch at 1770 cm$^{-1}$ in hexane solution. The mass spectrum (75 eV) shows peaks indicative of the ruthenium isotope pattern at $m/e$ 498 (M$^+$) and 402 (M$^+$ − CNCH$_2$CMe$_2$CH$_2$). These data are consistent with the product formulation Ru(DMPE)$_2$(CNCH$_2$CMe$_3$) which is formed in quantitative NMR yield (Table I).

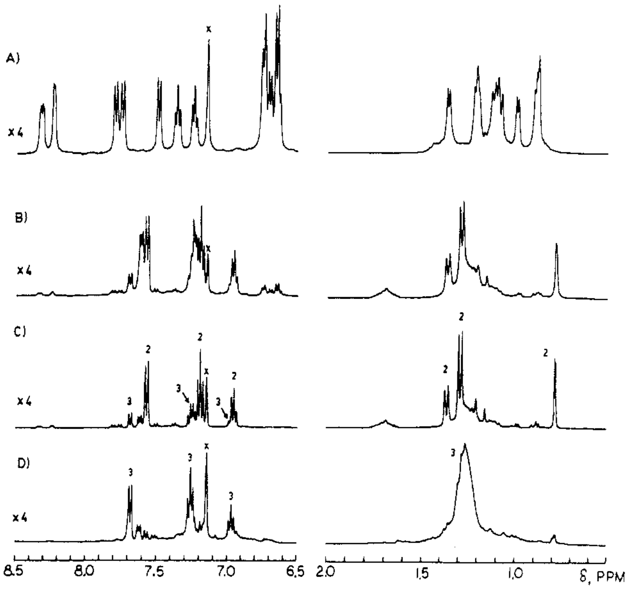
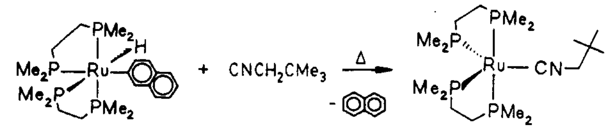


**Figure 1.** Reaction of Ru(DMPE)$_2$(naphthyl)H with phenyl isocyanide: (a) zero time; (b) after 20 h at 60 °C; (c) after removing volatiles at 40 °C; (d) after heating to 100 °C for 24 h. The peak labeled × is residual benzene.

As Ru(DMPE)$_2$(naphthyl)H is known to undergo reductive elimination of naphthalene at 60 °C,[7] Ru(DMPE)$_2$(CNCH$_2$CMe$_3$) is probably formed by a rate-determining loss of naphthalene followed by a trapping of the 16-electron coordinatively unsaturated intermediate [Ru(DMPE)$_2$] by the free isocyanide ligand (eq 1). No evidence for the formation of the intermediate benzene oxidative addition adduct Ru(DMPE)$_2$(C$_6$D$_5$)D was found in the $^1$H NMR spectrum. The same product is known to form from the reaction of Ru(DMPE)$_2$(PMe$_3$) with CNCH$_2$CMe$_3$.[8]



**1**

(1)

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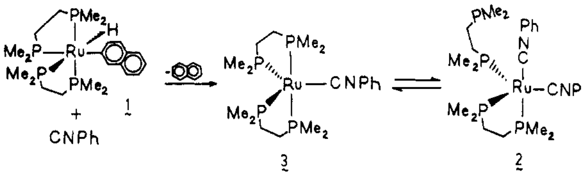
**B. Thermolysis of 1 with Phenyl Isocyanide.** A benzene solution (0.15 M) of 1 and ~2 equiv of phenyl isocyanide were heated at 60 °C for 20 h. The color of the solution was observed to gradually change from yellow to red. The multiplet for the phenyl resonance of the PhNC ($\delta$ 6.63–6.76) disappeared almost completely (0.18 equiv remaining), while approximately 25% of 1 remained. Many new resonances appeared in the aromatic region of the $^1$H NMR spectrum. Two doublets of doublets characteristic of naphthalene could be identified (Figure 1b). When the solvent was removed and the residue gently heated under vacuum, most of the naphthalene and all of the phenyl isocyanide could be removed from the nonvolatile ruthenium-containing products.

The $^1$H NMR spectrum of the nonvolatiles in $C_6D_6$ now showed two different phenyl resonances in the aromatic region, each characterized by a doublet and a pair of triplets in a 2:2:1 ratio (Figure 1c). The major product 2 displayed resonances at $\delta$ 7.569 (d, $J$ = 7.5 Hz), 7.195 (t, $J$ = 7.7 Hz), and 6.954 (t, $J$ = 7.3 Hz) in a 2:2:1 ratio, comprising 81% of the aromatic hydrogen. The minor product 3 displayed resonances at $\delta$ 7.682 (d, $J$ = 7.5 Hz), 7.263 (t, $J$ = 7.7 Hz), and 6.972 (t, $J$ = 7.3 Hz) in a 2:2:1 ratio, comprising 19% of the aromatic hydrogen. The aliphatic region of the spectrum showed three major doublets in a 1:2:1 ratio at $\delta$ 1.367 ($J$ = 8.5 Hz), 1.293 ($J$ = 7.6 Hz), and 0.785 ($J$ = 3.6 Hz), as well as several smaller broad multiplets. The large doublet at $\delta$ 0.785 integrates as 6 H relative to 4 H for the $\delta$ 7.569 doublet.

When the solution was warmed to 100 °C for 24 h, all of compound 2 was observed to be converted to 3 and several broad resonances appeared in the region $\delta$ 6.7–7.7. The aliphatic region of the spectrum displayed a single broad resonance ($\nu_{1/2}$ = 37 Hz) at $\delta$ 1.27 (Figure 1d).

The above observations are consistent with the initial formation of two different isocyanide complexes from 1 (eq 2). The major isomer formed with excess isocyanide,



(2)

2, is assigned the structure Ru($\eta^2$-DMPE)($\eta^1$-DMPE)-$(CNPh)_2$ on the basis of the $^1$H NMR spectrum. The aromatic resonances integrate for two phenyl groups relative to the resonance at $\delta$ 0.785, which can be assigned to the dangling $PMe_2$ portion of one of the DMPE ligands due to its high-field chemical shift and small P–H coupling constant. The remaining two doublets in a 1:2 ratio can be assigned to the remaining $PMe_2$ groups of the $\eta^1$-DMPE and the $\eta^2$-DMPE ligands, respectively. The five-coordinate d$^8$ molecule would be expected to be fluxional,[9] accounting for the equivalence of the isocyanide ligands.

The minor isomer 3 can be assigned the formula Ru$(DMPE)_2$(CNPh) and is is formed at the expense of 2 by dissociation of an isocyanide ligand. At 100 °C, slow polymerization of the free phenyl isocyanide to form indigo occurs,[10] eventually shifting the equilibrium from 2 to 3. Apparently, 3 is formed initially from 1 but then reacts rapidly with the excess isocyanide under the reaction conditions to form 2. Interestingly, no evidence for bis(isocyanide) complexes was seen with other isocyanides.

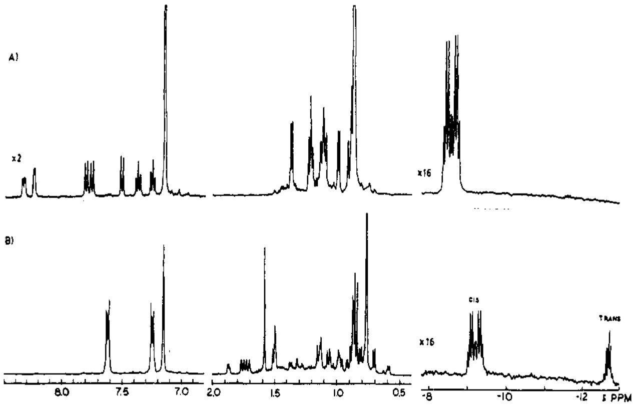


**Figure 2.** Reaction of Ru$(DMPE)_2$(naphthyl)H with *tert*-butyl isocyanide: (a) zero time. (b) after 24 h at 60 °C.

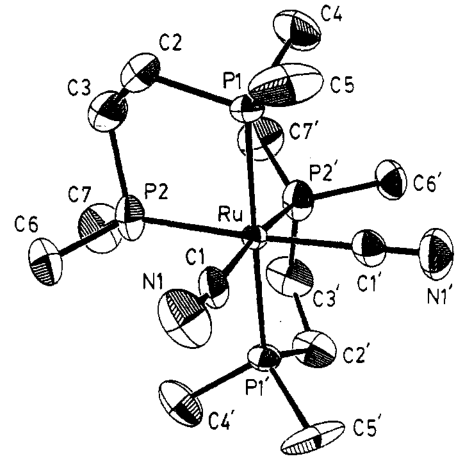


**Figure 3.** ORTEP drawing of Ru$(DMPE)_2(CN)_2$. Thermal ellipsoids are shown at the 50% probability level.

**C. Thermolysis of 1 in the Presence of Ethyl Isocyanide.** Upon thermolysis of a benzene solution of 1 at 60 °C in the presence of 1.1 equiv of ethyl isocyanide for 60 h, a similar monosubstitution product was formed. Resonances for 1 and free ethyl isocyanide ($\delta$ 0.509 (tt, $J$ = 7.2, 2.4 Hz, 3 H), 2.335 (qt, $J$ = 7.2, 1.9 Hz, 2 H)) were observed to decrease as those for naphthalene and coordinated ethyl isocyanide ($\delta$ 3.425 (q, $J$ = 7.8 Hz)) increased. A new broad singlet for the eight equivalent DMPE methyl groups in Ru$(DMPE)_2$(CNEt) appeared at $\delta$ 1.323. The NMR yield of Ru$(DMPE)_2$(CNEt) was close to quantitative, and a trace of ethylene (~10%; $\delta$ 5.241 (s)) was observed.

**D. Thermolysis of 1 in the Presence of *tert*-Butyl Isocyanide.** A benzene solution of 1 and *tert*-butyl isocyanide (4 equiv) were heated in a resealable tube at 60 °C for 22 h. While naphthalene was observed to appear by $^1$H NMR spectroscopy and virtually all of the free *tert*-butyl isocyanide ($\delta$ 0.867 (t, $J$ = 2.0 Hz) had disappeared, there was no evidence for a coordination complex of the *tert*-butyl isocyanide (Figure 2). White crystals deposited on the walls of the tube. A complicated pattern appeared in the DMPE region of the spectrum ($\delta$ 0.6–1.9), and two new hydride resonances appeared at $\delta$ −9.28 (dq, $J$ = 83, 24 Hz) and −12.75 (quint, $J$ = 22 Hz). Also observed was a large singlet at $\delta$ 0.767, a doublet at 0.856 ($J$ = 6.7 Hz), and broad singlets at $\delta$ 1.581 and 4.735. Identification of the products in this complex mixture was accomplished by removing the volatile (organic) portion of the reaction by vacuum distillation at 25 °C and analyzing the volatiles by gas chromatography.

The latter four resonances (plus those of naphthalene and unreacted *tert*-butyl isocyanide) were also found in the $^1$H NMR spectrum of the volatile portion of the re-

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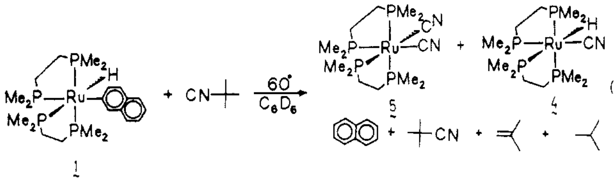
**Table II. Summary of Crystallographic Data for $Ru(DMPE)_2(CN)_2 \cdot H_2O$**

| | |
|---|---|
| Crystal Parameters | |
| formula | $RuP_4N_2C_{14}H_{32} \cdot H_2O$ |
| fw | 471.41 |
| cryst system | orthorhombic |
| space group | Pccn |
| $Z$ | 4 |
| $a$, Å | 9.2842 (14) |
| $b$, Å | 14.1091 (30) |
| $c$, Å | 16.3641 (50) |
| $V$, Å$^3$ | 2143.6 (1.4) |
| $d_{calcd}$, g/cm$^3$ | 1.46 |
| cryst dimens, mm | 0.20 × 0.18 × 0.08 |
| temp, °C | 25 |
| Measurement of Intensity Data | |
| diffractometer | Enraf-Nonius CAD4, $\kappa$ geometry |
| radiatn (monochromator) | Mo, 0.71073 Å (graphite) |
| scan type | $2\theta/\omega$ |
| scan range, deg | $0.7 + 0.35 \tan \theta$ |
| scan rate, deg/min | 1.2-20 |
| total background time | scan time/2 |
| takeoff angle, deg | 2.6 |
| $2\theta$ range, deg | 2-45 |
| data collected | $+h,+k,+l$ |
| no. of data collected | 1399 |
| no. of unique data $>3\sigma$ | 967 |
| no. of parameters varied | 101 |
| abs coeff, cm$^{-1}$ | 14.386 |
| systematic absences | $0kl$, $l$ odd; $h0l$, $l$ odd; $hk0$, $h$ + k odd |
| $R_1$ | 0.0498 |
| $R_2$ | 0.0660 |
| goodness of fit | 2.27 |

action and can be assigned to trimethylacetonitrile, isobutane, and isobutene, respectively, by comparison with authentic samples. Quantitative gas chromatographic analysis of this sample shows the formation of the three organic products in ~120%, 54%, and 83%, respectively, based on ruthenium (eq 3).



(3)

The nonvolatile portion of the reaction corresponded to a 11:1 mixture of the known compounds, *cis*- and *trans*-$Ru(DMPE)_2(CN)H$ (**4**), identified by their characteristic $^1H$ NMR spectra (Table I).[7] Integration of the hydride resonances relative to naphthalene gave a 70% yield of the combined isomeric products.

The remaining white crystalline product (30%) was identified as the dicyanide complex *cis*-$Ru(DMPE)_2(CN)_2$ (**5**) on the basis of spectroscopic, analytical, and X-ray data. The $^1H$ NMR spectrum in acetone-$d_6$ showed four resonances of equal intensity for the pairs of distinct DMPE methyl groups at $\delta$ 1.398 (d, $J$ = 6.8 Hz), 1.488 (d, $J$ = 7.9 Hz), 1.525 (t, $J$ = 2.7 Hz), and 1.741 (t, $J$ = 3.9 Hz). The $^{31}P$ NMR showed two triplets of equal intensity at $\delta$ -13.6 ($J$ = 23 Hz) and -6.0 ($J$ = 23 Hz). The mass spectrum (75 eV) displayed a strong parent ion at $m/e$ 454, and the infrared spectrum showed a single band at 2085 cm$^{-1}$ with a shoulder at 2075 cm$^{-1}$.

**Table III. Selected Distances (Å) and Angles (deg) in $Ru(DMPE)_2(CN)_2$**

| | | | | | |
|---|---|---|---|---|---|
| Ru-P1 | 2.319 (2) | P1-Ru-P1′ | 176.8 (1) | P1-Ru-C1 | 89.4 (2) |
| Ru-P2 | 2.321 (2) | P2-Ru-P2′ | 94.0 (1) | P1-Ru-C1′ | 88.3 (2) |
| Ru-C1 | 2.045 (8) | P1-Ru-P2 | 96.65 (7) | P2-Ru-C1 | 88.9 (2) |
| C1-N1 | 1.130 (9) | P1-Ru-P2′ | 85.55 (7) | P2-Ru-C1′ | 174.5 (2) |
| | | C1-Ru-C1′ | 88.7 (4) | Ru-C1-N1 | 177.8 (7) |

**Table IV. Positional Parameters for $Ru(DMPE)_2(CN)_2$[a]**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Ru | 0.250 | 0.250 | 0.15094 (6) | 1.65 (2) |
| P1 | 0.1516 (3) | 0.4010 (2) | 0.1549 (2) | 2.46 (5) |
| P2 | 0.4261 (3) | 0.2824 (2) | 0.0542 (2) | 3.64 (6) |
| O1 | 0.250 | 0.750 | 0.1278 (9) | 7.7 (4) |
| N1 | 0.474 (1) | 0.3101 (7) | 0.2879 (5) | 5.0 (2) |
| C1 | 0.392 (1) | 0.2886 (7) | 0.2403 (6) | 2.8 (2) |
| C2 | −0.023 (1) | 0.4032 (8) | 0.1010 (7) | 4.5 (3) |
| C3 | 0.504 (1) | 0.1642 (8) | 0.0192 (8) | 5.3 (3) |
| C4 | 0.252 (2) | 0.4989 (7) | 0.1075 (8) | 5.4 (3) |
| C5 | 0.111 (2) | 0.4504 (8) | 0.2552 (7) | 5.8 (3) |
| C6 | 0.591 (1) | 0.3446 (8) | 0.0867 (7) | 4.1 (3) |
| C7 | 0.401 (1) | 0.334 3(9) | −0.0466 (7) | 5.7 (3) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

A single crystal of colorless **5** grown from acetone solution in air was subjected to X-ray analysis on a CAD-4 diffractometer, revealing an orthorhombic cell with absences for space group *Pccn*. A Patterson map revealed the location of the Ru on a twofold axis. Subsequent difference Fourier maps showed the remaining unique atoms of **5** in a cis-octahedral configuration, plus a water of crystallization on a distinct twofold axis. Parameters for data collection and refinement are given in Table II. Table III gives selected distances and angles, and Table IV lists atomic coordinates.

The effect of $t$-BuNC concentration on the reaction was investigated by 60 °C thermolysis of 0.02 M solutions of **1** containing 0.75, 1.5, and 3.9 equiv of $t$-BuNC. $^1H$ NMR examination of the solutions after 8 and 18 h revealed identical percentages of all products, indicating that the product ratios are independent of [$t$-BuNC].

A benzene solution of **4** and isobutylene was heated to 60 °C overnight. No reaction was observed. The isobutane is apparently not formed from isobutylene and the HCN complex in a secondary reaction.

## Discussion

The previous studies of $Ru(DMPE)_2$(naphthyl)H indicate that the molecule thermally undergoes reductive elimination of naphthalene to generate the unstable coordinatively unsaturated species [$Ru(DMPE)_2$] that is capable of oxidatively adding to a host of aromatic and acidic C-H bonds.[7] The initial object of this study was to determine if isocyanides could be used in conjunction with the catalytic C-H activation capability of $Ru(DMPE)_2$(aryl)H to convert aromatics plus isocyanides into aldimines.[11] One potential problem anticipated with this scheme is the ability of an isocyanide, a strong $\pi$-acceptor, to coordinate irreversibly to the low-valent ruthenium center.

As presented above, isocyanides do indeed coordinate strongly to [$Ru(DMPE)_2$], and competitive activation of benzene solvent is not observed. The observation of formation of **2** from **1** plus PhNC implies that the initially formed **3** undergoes reversible dissociation of one end of a chelating dmpe ligand. The isocyanide in solution apparently competes with the closure of the $\eta^1$-DMPE chelate in the formation of **2**. The preference of the low-valent Ru(0) for $\pi$-acceptor ligands probably drives this equilibrium toward **2**. Labilization of one end of a chelating ligand in substitution reactions of chelating bis(amines)

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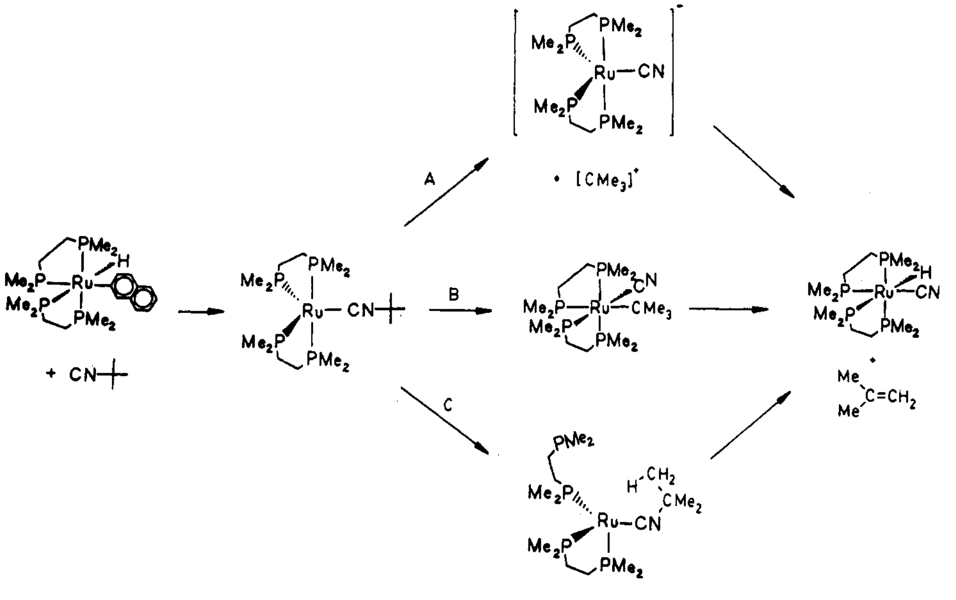
[11] For the reaction $C_6H_6 + CH_3NC = C_6H_5CH{=}NCH_3$, $\Delta G° \approx -7$ kcal/mol.

**Scheme I**



and bis(phosphines) has also been observed by Dobson.[12]

An interesting side reaction of some coordinated isocyanides possessing $\beta$-hydrogens was found to occur. The reaction formally involves $\delta$-elimination of the isocyanide C–H bond with concomitant cleavage of the isocyanide C–N single bond, producing an olefin and a metal hydrido cyanide complex.

The cleavage of isocyanide C–N single bonds by transition metals, while not unprecedented, is quite rare. Lippard has recently reported the dealkylation of $[M(CN\text{-}t\text{-}Bu)_7]^{2+}$ (M = Mo, W) in refluxing ethanol in low yield.[5a] Although the fate of the *tert*-butyl group was not determined (eq 4), it was proposed to have formed either

$$[Mo(CNt\text{-}Bu)_7]^{2+} \xrightarrow{ROH} [Mo(CNt\text{-}Bu)_6(CN)]^+ \begin{bmatrix} +\ t\text{-}Bu\text{-}OR \\ \text{or}\ Me_2C{=}CH_2 \end{bmatrix} \quad (4)$$

*tert*-butyl alcohol or isobutylene. Tschugaeff and Teearu reported the formation of $Pt(CN\text{-}t\text{-}Bu)_2(CN)_2$ upon dissolving $[Pt(CN\text{-}t\text{-}Bu)_4]^{2+}$ in methanol,[5c] and the cleavage of a C–N single bond is almost certainly involved in the alkylation of $[Fe(CNCH_2Ph)_5(CN)]^+$ with benzyl bromide.[13]

As the onset of reaction of *tert*-butyl isocyanide with **1** occurs at 60 °C, the temperature at which naphthalene is lost from the molecule, the initial formation of $Ru(DMPE)_2(CN\text{-}t\text{-}Bu)$ (**6**) seems quite likely. The intermediacy of *tert*-butyl carbonium ions in the reaction might seem to be a reasonable way to account for the dehydrocyanation reaction (Scheme Ia) and has precedence in the literature on *tert*-butyl isocyanide.[14] The formation of a major product of the reaction, trimethylacetonitrile, is unaccounted for however. An independent mechanism involving a simple [1,2] shift of the *tert*-butyl group could be invoked. This type of rearrangement does not occur in the absence of the ruthenium but is known to occur in the presence of Lewis acids.[15] The 16-electron intermediate $[Ru(DMPE)_2]$ could certainly act as a Lewis acid by coordinating to the *t*-BuNC carbon as it does with other isocyanides.

An alternative mechanism for the formation of the products would be to invoke a [1,3] shift of the *tert*-butyl group to the ruthenium metal center following complexation (Scheme Ib). While there is no evidence for such an alkyl cyanide intermediate and no precedent for this type of migration, the formation of this species does result in the two electron oxidation of the electron rich Ru(0) center and maintains an 18-electron configuration. Trimethylacetonitrile could then be formed by reductive elimination, and isobutylene plus **4** by a competitive $\beta$-elimination. With this mechanism the formation of benzonitrile from **1** plus phenyl isocyanide would have been expected due to the superior migrating ability of the phenyl group. The lack of rearrangement product argues against this pathway.

A third possible mechanism invokes the dissociation of one of the $\eta^2$-DMPE ligands to $\eta^1$ coordination in complex **6**, as occurs with phenyl isocyanide (Scheme Ic). Subsequent intramolecular $\delta$-elimination directly produces **4** plus isobutylene. While this 6-membered transition state might be thought to be highly strained due to the expected linearity of the Ru–C–N–C linkage, $\pi$-back-bonding of the CNR would tend to bend the C–N–C angle, bringing the $\delta$-hydrogens closer to the metal. The low energy and large width of the $\nu_{C\equiv N}$ IR stretch supports this notion.[16]

The observation of ethylene from the reaction of **1** with EtNC is inconsistent with mechanism Ia, since a primary ethyl carbonium ion would be involved. On the other hand mechanism Ic would permit intramolecular elimination of ethylene, with the lower extent of dehydrocyanation compared to *t*-BuNC being attributable to a *gem*-dimethyl effect accelerating the elimination with the latter substrate.[17] Again, an independent pathway must be involved for the formation of trimethylacetonitrile.

In any of the above mechanisms, the formation of isobutane remains unknown but can be accounted for by the

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[12] Dobson, G. R.; Binzet, N. S. *J. Coord. Chem.* **1984**, *13*, 153–157. Dobson, G. R.; Mansour, S. E.; Halverson, D. E.; Erikson, E. S. *J. Am. Chem. Soc.* **1983**, *105*, 5505–5506. Dobson, G. R.; Dobson, C. B.; Halverson, D. E.; Mansour, S. E. *J. Organomet. Chem.* **1983**, *253*, C27–C32.

[13] Heldt, W. Z. *J. Inorg. Nucl. Chem.* **1962**, *24*, 265–274.

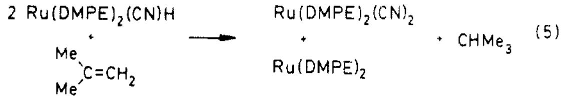
[14] The formation of a *tert*-butyl carbonium ion by leaving group dissociation has ample precedent: Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*; Harper and Row: New York, 1976; pp 216, 375–377. Saunders, W. H.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973 and references therein.

[15] Milich, F. *Chem. Rev.* **1972**, *72*, 101–113 and references therein.

[16] Other studies in our lab indicate that intramolecular activation occurs with 2,6-xylyl isocyanide (Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.*, in press.

[17] Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701–704. Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856–3857. Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972–1982.

overall stoichiometry shown in eq 5. Two molecules of



$$2\,\mathrm{Ru(DMPE)_2(CN)H} + \mathrm{Me_2C{=}CH_2} \longrightarrow \mathrm{Ru(DMPE)_2(CN)_2} + \mathrm{Ru(DMPE)_2} + \mathrm{CHMe_3} \quad (5)$$

**4** can hydrogenate one molecule of isobutylene, producing one molecule of **5** and one molecule of the coordinatively unsaturated intermediate [Ru(DMPE)$_2$], which reenters the cycle. While this stoichiometry applies to the reaction, it is not responsible as written for the isobutane formation. The observed stoichiometry balances in that the combined yields of isobutene plus isobutane is equal to the number of equivalents of cyanide bound to ruthenium (**4** + 2 × **5**).

## Conclusions

The formation of isocyanide complexes of low-valent metals is apparently a rapid process, yielding a strong metal–isocyanide bond. In certain cases, the alkyl group of the isocyanide is activated toward cleavage of the C–N single bond, this activation being favored by both the oxidation of the electron-rich metal and the formation of a metal–cyanide bond. While the exact mechanism of the cleavage reaction is not certain, evidence points toward a concerted $\delta$-elimination to produce an HCN complex and an olefin (dehydrocyanation). The low-valent metal acts not only as a $\pi$-donor to the isocyanide ligand but also as a $\sigma$-acceptor (Lewis acid) as evidenced by the catalysis of the rearrangement of *tert*-butyl isocyanide to trimethylacetonitrile. The chelating DMPE ligand is also labilized by isocyanide coordination. Other metals are under evaluation for this unusual capability to cleave strong C–N bonds.

## Experimental Section

All solvents were distilled from dark purple solutions of sodium benzophenone ketyl under a nitrogen atmosphere. All compounds were handled in a Vacuum Atmospheres Dri-Lab. All experiments were performed in sealed NMR tubes or ampules prepared and degassed on a high vacuum line. *tert*-Butyl isocyanide and all organic amines were purchased from Aldrich Chemical Co. Phenyl isocyanide was prepared by using the method of Ugi.[18] Ethyl isocyanide was prepared by treatment of silver cyanide with ethyl iodide.[4a] Ru(DMPE)$_2$(naphthyl)H was prepared according to the literature method.[7] $^1$H NMR spectra were recorded on a Bruker WH-400 NMR spectrometer.

**Preparation of Neopentyl Isocyanide.** Neopentyl formamide (12 g, 0.104 mol), 50 mL of quinoline, and 25 mL of pentane were placed in a flask at 0 °C. POCl$_3$ (5.6 mL, 0.060 mol) was added dropwise with vigorous stirring. The mixture was heated gently for several minutes and the white mass that formed treated with 75 mL of H$_2$O. The pentane layer was separated and the aqueous portion extracted wth pentane (3 × 15 mL). The combined extracts were washed with 0.01 N HCl (2 × 10 mL) and saturated aqueous Na$_2$CO$_3$ (2 × 10 mL). The solution was dried over MgSO$_4$ and then distilled through a vigreaux column. The fraction boiling at 120–122 °C was collected and contained 3.2 g (33%) of neopentyl isocyanide contaminated with a small (<5%) amount of pentane.

**Reaction of Ru(DMPE)$_2$(naphthyl)H (1) with Neopentyl Isocyanide.** A benzene solution (2 mL) of **1** (106 mg, 0.20 mmol) and neopentyl isocyanide (44 mg, 0.25 mmol) were placed in a drawn out test tube, freeze–pump–thaw–degassed on the vacuum line, and sealed under vacuum. The light yellow solution was heated at 60 °C for 45 h and then transferred into a sublimation apparatus under a nitrogen atmosphere. After careful removal of the solvent and naphthalene at 25 °C (10$^{-4}$ mm), the product was sublimed at 75 °C; isolated yield 65 mg (67%). Mass spectrum (75 eV): calcd for RuP$_4$NC$_{18}$H$_{43}$, *m/e* 498.51; found, *m/e* 498.3 ± 0.5, 428, 402.

In a separate experiment, 50 mg of **1** (0.94 mmol) and 19 $\mu$L of neopentyl isocyanide (0.19 mmol) were placed in an NMR tube attached to a ground glass joint and 0.6 mL of C$_6$D$_6$ was added by vacuum distillation. The tube was sealed and then heated to 60 °C for 18 h. An NMR spectrum revealed virtually quantitative yield of a new product with resonances at $\delta$ 3.257 (s, 2 H), 1.078 (s, 9 H), and 1.330 (br s, ~34 H), plus naphthalene. The reaction was only 11% complete after 2 h.

**Reaction of 1 with Phenyl Isocyanide.** **1** (50 mg, 0.0945 mmol) and 20 $\mu$L (0.19 mol) of phenyl isocyanide were placed in an NMR tube attached to a ground glass joint and C$_6$D$_6$ condensed into the tube (0.6 mL). The tube was sealed under vacuum and heated to 60 °C for 20 h, as the color of the solution changed slowly from light yellow to red. A $^1$H NMR spectrum revealed that the resonances for the starting complex **1** had been replaced by resonances for several new products (see text). The solution was transferred to a flask, and the volatiles were removed by vacuum distillation on the vacuum line (40 °C (10$^{-4}$ mm)). C$_6$D$_6$ was added to the residue and its NMR spectrum recorded, showing a mixture of products (see text), but very little naphthalene. The sample was heated to 100 °C for 24 h and the $^1$H NMR recorded, showing the conversion of the mixture of products to a single product. IR (THF): 1680 (s), 1580 (m) cm$^{-1}$.

**Reaction of 1 with Ethyl Isocyanide.** Ethyl isocyanide (3.7 $\mu$L, 0.050 mmol) and **1** (22 mg, 0.042 mmol) were sealed in an NMR tube on the vacuum line along with 0.4 mL of C$_6$D$_6$. The tube was heated to 60 °C for 60 h and a $^1$H NMR spectrum recorded, showing naphthalene, a new product identified as Ru(DMPE)$_2$(CNEt) (~100% based upon integration of the EtNC methylene resonance vs. naphthalene), and a small amount of ethylene (~10%; $\delta$ 5.241).

**Reaction of 1 with *tert*-Butyl Isocyanide.** **1** (65 mg, 0.12 mmol) was weighed into an NMR tube attached directly to a Teflon valve and 54 $\mu$L (4 equiv) of *tert*-butyl isocyanide plus 0.8 mL of C$_6$D$_6$ introduced by vacuum distillation (25 °C (10$^{-4}$ mm)). The sealed tube was heated to 60 °C for 22 h, and white crystals were observed to deposit in the tube. A $^1$H NMR spectrum showed the disappearence of **1** and the appearance of many new resonances, most notably, naphthalene. The other products were identified as trimethylacetonitrile ($\delta$ 0.767 (s); ~150% based on free naphthalene), isobutylene ($\delta$ 4.745 (br s, 2 H), 1.581 (br s, 6 H); 76% based on free naphthalene), isobutane ($\delta$ 0.856 (d, $J$ = 6.7 Hz, 9 H); could not be integrated), and an 11:1 mixture of *cis*- and *trans*-**4** (Table I).

The white crystals of **5** were collected by filtration and recrystallized from acetone in air. The complex crystallizes with one water of crystallization (30% yield). Anal. Calcd for RuP$_4$N$_2$C$_{14}$H$_{32}$·H$_2$O: C, 35.67; H, 7.27; N, 5.94. Found: C, 35.74; H, 7.26; N, 6.17. Mass spectrum (75 eV): *m/e* 454 (Ru isotope pattern). IR (KBr): 2966 (m), 2904 (m), 2102 (s), 1423 (m), 1290 (w), 938 (s), 908 (m), 849 (w), 720 (w) cm$^{-1}$.

The reaction was analyzed for the products isobutene, isobutane, and trimethylacetonitrile by expansion of the volatiles from the entire reaction mixture into an evacuated chamber (volume ≈ 5 L). The gas mixture was then analyzed by GC on two columns by using added diethyl ether as an internal standard. A 10% ODPN/Chrom WAW column at 60 °C was used to determine the yield of trimethylacetonitrile (0.144 mmol), and a 10% EDO-1/Chrom P AW column at 20 °C was used to determine the yields of isobutene (0.100 mmol) and isobutane (0.065 mmol).

**Effect of *t*-BuNC Concentration on Rate and Product Distribution.** Three samples of 10 mg of **1** (0.019 mmol) in 1 mL of C$_6$D$_6$ containing 1.6 $\mu$L (0.014 mmol), 3.2 $\mu$L (0.028 mmol), and 8.5 $\mu$L (0.085 mmol) of *t*-BuNC, respectively, were sealed under vacuum in NMR tubes. $^1$H NMR spectra were recorded after thermolysis at 60 °C for 8 and 18 h. All reactions showed identical percentages of products.

**X-ray Structural Determination of Ru(DMPE)$_2$(CN)$_2$.** Well-formed colorless crystals of the compound were prepared by slow evaporation of an acetone solution in air. The lattice constants were obtained from 25 centered reflections with values of $\chi$ between 10 and 45°. Cell reduction with the program TRACER revealed a primative orthorhombic crystal system. Data were collected on the crystal in accord with the parameters in Table

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[18] *Organic Syntheses*; Wiley: New York, 1973; *Coll.* Vol. 5, pp 1060–1063.

II. The space group was uniquely assigned as *Pccn* (No. 56) on the basis of the systematic absences (0*kl*, *l* odd; *h*0*l*, *l* odd; *hk*0, $h + k$ odd), and the correctness of this choice was confirmed by successful solution of the Patterson map, showing a ruthenium atom on one of the two twofold axes. The Molecular Structure Corp. and Enraf-Nonius SDP programs were used for solution and refinement of the structure.[19] Least-squares refinement of the ruthenium followed by a difference Fourier map revealed four peaks for the DMPE phosphorus atoms. Introduction of two of these peaks not related by an apparent mirror plane revealed all 11 non-hydrogen atoms in a subsequent difference Fourier map. Anisotropic refinement of all 11 atoms converged at $R_1 = 0.080$. A difference Fourier map showed a single large peak on an independent twofold axis corresponding to the oxygen atom of a water molecule (5.8 e/Å$^3$), apparently picked up from the atmosphere during recrystallization. Final refinement was carried out on all 12 atoms giving $R_1 = 0.0498$ and $R_2 = 0.0660$. Table III contains relevant bond distances and angles and Table IV positional parameters.

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**Registry No.** 1, 60938-49-0; 2, 103190-62-1; 3, 103190-63-2; *cis*-4, 68878-59-1; *trans*-4, 68907-31-3; 5, 103190-64-3; $Ru(DMPE)_2(CNEt)$, 103190-65-4; $Ru(DMPE)_2(CN)_2 \cdot H_2O$, 103190-66-5; $Ru(DMPE)_2(CHCH_2CMe_3)$, 101519-29-3; $POCl_3$, 10025-87-3; neopentyl formamide, 78257-53-1; neopentyl isocyanide, 72243-18-6; phenyl isocyanide, 931-54-4; ethyl isocyanide, 624-79-3; *tert*-butyl isocyanide, 7188-38-7; trimethylacetonitrile, 630-18-2; isobutylene, 115-11-7; isobutane, 75-28-5.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and bond distances and angles (3 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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[19] $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum wF_o^2\}$, where $w = \{\sigma^2(F_o) + [\rho F_o^2]^2\}^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of Scattering Factors $f_o, f', f''$: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV Table 2.2B and 2.3.1.

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# Dynamic Behavior of the Flyover Bridge Complexes $M_2(CO)_5L\{\mu\text{-}[C(R)=C(R')]_2CO\}$ (M = Ru, Fe; L = CO, $PPh_3$, $AsPh_3$, $SbPh_3$; R, R′ = Me, Ph)

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The variable-temperature $^1H$ and $^{13}C$ NMR studies of a series of isomeric "flyover bridge" complexes $M_2(CO)_5L\{\mu\text{-}[C(R)=C(R')]_2CO\}$ (M = Ru, Fe; L = CO, $PPh_3$, $AsPh_3$, $SbPh_3$; R, R′ = Me, Ph) show that a fluxional process of the dienone ligand, leading to the exchange of σ- and π-bonds at the two metal centers is occurring in these compounds on the NMR time scale. The activation energy for this process in the entire series is essentially invariant ($\Delta G^{\ddagger} = (70\text{–}76) \pm 5$ kJ/mol) with the nature of M and L and is apparently independent of localized carbonyl exchange at each $M(CO)_3$ unit.

## Introduction

In the last 15 years several studies concerning the intramolecular exchange of CO groups in metal carbonyl derivatives have been reported and a variety of rearrangement modes of these ligands has been shown to occur in this class of molecules.[1] Relatively less attention has been devoted to the study of the mobility of other organic ligands in these molecules. However, some novel fluxional processes have already been reported to take place on the NMR time scale. For instance, a low-energy σ–π exchange process of the bridging vinyl group in $HOs_3(CO)_{10}(CH{=}CH_2)$ was reported by Shapley et al.,[2] and, more recently, we have shown that a "wagging" motion of the allene ligand (coupled with the "hopping" motion of the hydride on different edges of the $M_3$ triangle) is occurring in related $HM_3(CO)_9$(allene) (M = Ru, Os) systems.[3]

It has also been shown, by the use of chiral derivatives, that the formal rotation of the M–M and C–C bond vectors is occurring in the $(\mu_2\text{-}\eta^2)M_2$(alkyne) complexes[4] as well as

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[1] Cotton, F. A.; Hanson, R. E. In *Rearrangements in Ground and Excited States*; Academic Press: New York, 1980; Vol. 2, p 379.

[2] Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *95*, C43.

[3] Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E.; Organometallics **1982**, *1*, 640.