by the Evans method gave a μ_{eff} value of 2.20 at 293 K.[15]

The electronic spectrum of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ (**2**) exhibits a low-energy band at 819 nm (ϵ = 1770 M^{-1} cm^{-1}), presumably due to a low-energy d–d transition on the basis of the extinction coefficient. Several higher energy bands appear at λ_{max}, nm (ϵ) = 546 (630), 319 (22 400), 257 (56 500). A cyclic voltammogram of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ in 0.1 M $(TBA)BF_4$–CH_2Cl_2 shows a reversible couple at $E_{1/2}$ = –0.04 V vs Ag/AgCl, corresponding to a one-electron reduction to Rh(I).[16] Not surprisingly, this process is shifted to more positive potentials relative to that of $[Rh(\eta^3\text{-}TMPP)_2][BF_4]_2$ (**1**) due to the electron-withdrawing effect of the π-acceptor ligands.[17] The Rh(II)/Rh(I) couple falls at a potential less positive than the Rh(II)/Rh(III) couple for the parent complex, $[Rh(\eta^3\text{-}TMPP)_2]^{2+}$ (cation of **1**), however, and as a result, $[Rh(TMPP)_2(CNBu^t)_2]^{2+}$ is stable with respect to spontaneous reduction to Rh(I) in the presence of $[Rh(\eta^3\text{-}TMPP)_2]^{2+}$. This is in sharp contrast to the situation in the analogous $[Rh(\eta^3\text{-}TMPP)_2]^{2+}$/carbon monoxide chemistry.[8] Compound **2**, in fact, can be chemically reduced in the presence of cobaltocene to give the yellow Rh(I) complex $[Rh(TMPP)_2(CNBu^t)_2][BF_4]$ (**4**). The infrared spectrum of **4** shows a strong band, ν(CN) = 2118 cm^{-1}, shifted to lower energy than the corresponding stretch in **2** due to increased back-bonding upon reduction from Rh(II) to Rh(I).

It is worth mentioning at this point that similar reactions of **1** with the less bulky isocyanides CNMe and $CNPr^i$ were also carried out. The $CNPr^i$ chemistry proceeds exactly as the $CNBu^t$ reaction, leading to the formation of a stable Rh(II) species, but in the case of MeNC, no stable Rh(II) adducts could be isolated; instead, the reaction mixture contained several diamagnetic species, probably Rh(I) and Rh(III) by analogy to the CO chemistry. Since methyl isocyanide and carbon monoxide are very similar in size as well as π-accepting capabilities, it is not possible to draw any firm conclusions about the influence of the different R groups in the isocyanide chemistry, but the results suggest that electronic factors as well as steric factors play a role in the stabilization of these mononuclear Rh(II) complexes.

The title compound represents the first mononuclear organometallic Rh(II) complex to be fully characterized.[18] Reactivity studies of $[Rh(TMPP)_2(CNBu^t)_2][BF_4]_2$ with a variety of substrates are in progress and will be published in due course.

Acknowledgment. We gratefully acknowledge the National Science Foundation (PI Grant CHE-8914915) and Michigan State University (Research Initiation Grant) for providing funding for this work. We thank Dow Chemical Co. and Michigan State University College of Natural Science for Research Fellowships for S.C.H. We also acknowledge Johnson Matthey for a generous loan of $RhCl_3 \cdot xH_2O$. X-ray equipment was supported by grants from the National Science Foundation (Grants CHE-8403823 and CHE-89080088).

Registry No. **1**, 121757-68-4; **2**, 139426-71-4; **3**, 139426-72-5.

Supplementary Material Available: Tables of crystallographic parameters, atomic positional and thermal parameters, all bond distances and angles, and anisotropic thermal parameters (35 pages); a listing of structure factors (91 pages). Ordering information is given on any current masthead page.

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[15] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* **1969**, *46*, 167.

[16] Cyclic voltammogram in 0.1 M $[(Bu^n)_4N][BF_4]$–CH_2Cl_2 at a scan rate of 200 mV s^{-1} using a Pt-disk working electrode and a Ag/AgCl reference electrode. Under the same conditions the ferrocene/ferrocenium couple occurs at +0.46 V.

[17] Dunbar, K. R.; Walton, R. A. *Inorg. Chim. Acta* **1984**, *87*, 185.

[18] Note added in proof: Recently, the synthesis and X-ray structure of a stable mononuclear Rh(II) aryl complex was reported: Hay-Motherwell, R. S.; Koschmieder, S. U.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2821.

Intramolecular Hydride Migration from Formyl to Carbonyl and Nitrene Ligands

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Summary: Reaction of $[Tp'W(CO)_2(NPh)][PF_6]$ [Tp' = hydrotris(3,5-dimethylpyrazolyl)borate] with lithium borohydride at –40 °C generates Tp'W(CO)(NPh)(CHO) (**1**), which undergoes hydride migration from carbon to nitrogen (at –70 °C, k_{obs} = 7.2 × 10^{-6} s^{-1}, $\Delta G^{\ddagger}$ = 16.5 kcal/mol, $t_{1/2}$ = 27 h) to form $Tp'W(CO)_2(NHPh)$. Crossover experiments indicate that the hydride migration is intramolecular. The metal formyl intermediate is fluxional; hydride migration interconverts the formyl and carbonyl ligands. The rate constant for this degenerate migration is 40 s^{-1} at –41 °C with $\Delta G^{\ddagger}$ = 11.7 kcal/mol. The analogous acyl complex Tp'W(CO)(NPh)[C(O)Ph] (**3**) has been synthesized from the reaction of $[Tp'W(CO)_2(NPh)][PF_6]$ with PhMgBr.

We previously observed that the nitrene complex $[Tp'W(CO)_2(NPh)][PF_6]$ can be synthesized by hydride abstraction from the amido complex $Tp'W(CO)_2(NHPh)$ with $[Ph_3C][PF_6]$.[1] Conversely, treatment of $[Tp'W(CO)_2(NPh)][PF_6]$ with lithium borohydride in acetonitrile at –40 °C results in re-formation of the amido complex, $Tp'W(CO)_2(NHPh)$. We now report mechanistic studies which indicate that hydride initially attacks at a carbonyl carbon to yield a formyl complex, Tp'W(CO)(NPh)(CHO) (**1**). The amido complex is subsequently formed by intramolecular hydride migration from carbon to nitrogen. This chemistry calls to mind the prediction by Fenske and Milletti[2a] that hydride attack occurs at the nitrosyl ligand in $[CpRe(NO)(CO)(PPh_3)]^+$ even though only the formyl product, $CpRe(NO)(CHO)PPh_3$, has ever been observed.[2b]

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[1] Luan, L.; White, P. S.; Brookhart, M. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190.

[2] (a) Fenske, R. F.; Milletti, M. C. *Organometallics* **1986**, *5*, 1243. (b) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

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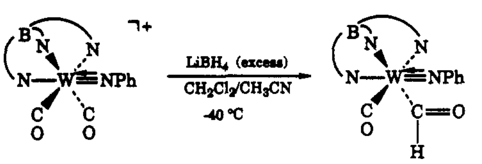
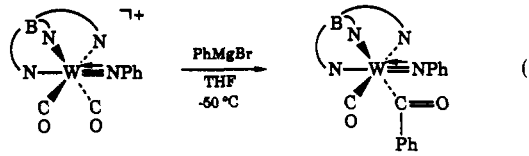
The reaction of $[Tp'W(CO)_2(NPh)][PF_6]$ with a large excess of lithium borohydride (eq 1) at −40 °C in acetonitrile/methylene chloride (3:1) affords a single product in quantitative yield as monitored by ^{1}H NMR spectroscopy.[3] A 1:1:1 pattern is observed for the three pyrazole protons, which indicates that the molecular mirror plane characterizing the reagent and the product is absent in this intermediate. Formation of a neutral formyl complex[4,5] is suggested by an ^{1}H NMR signal which integrates for one proton at 16.5 ppm ($^2J_{WH}$ = 20 Hz). Confirmation of formyl formation was provided by the ^{13}C NMR spectrum when ^{13}C-labeled $[Tp'W(^*CO)_2(NPh)][PF_6]$ (33% enrichment) was used as the reagent. The terminal carbonyl carbon and the formyl carbon of the intermediate are located downfield with *C*O at 259 ppm and *C*HO at 293 ppm ($^1J_{HC}$ = 132 Hz) in acetonitrile.[4] The infrared spectrum of the intermediate shows one strong absorption at 1948 cm^{-1} (the terminal carbonyl) and a weak absorption at 1680 cm^{-1} (formyl carbonyl).[4]

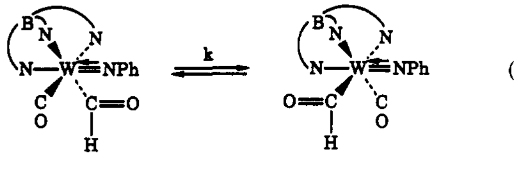


(1)

Support for the feasibility of hydride attack at a carbonyl carbon is provided by the analogous acyl complex $Tp'W(CO)(NPh)[C(O)Ph]$ (3), which formed when $[Tp'W(CO)_2(NPh)][PF_6]$ was treated with PhMgBr in THF at −50 °C (eq 2). The acyl complex **3** has been isolated in good yield as brown crystals. Spectroscopic data for **3** and the formyl complex $Tp'W(CO)(NPh)(CHO)$ are similar. The infrared spectrum of **3** exhibits a strong absorption at 1937 cm^{-1} for the terminal carbonyl. The ^{1}H NMR spectrum shows three singlets for the pyrazole protons. The terminal carbonyl carbon and the acyl carbon are located at 274 ppm ($^1J_{WC}$ = 167 Hz) and 286 ppm ($^1J_{WC}$ = 133 Hz), respectively. The observation of a two-bond tungsten coupling of 19 Hz to the ipso carbon of the nitrene *N*-phenyl group in the acyl complex is diagnostic for a $W{\equiv}N{-}C_6H_5$ unit.[1,6]

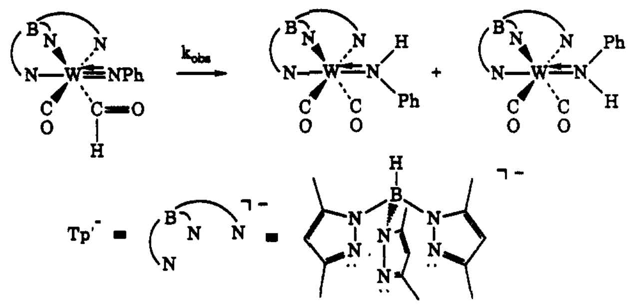


(2)

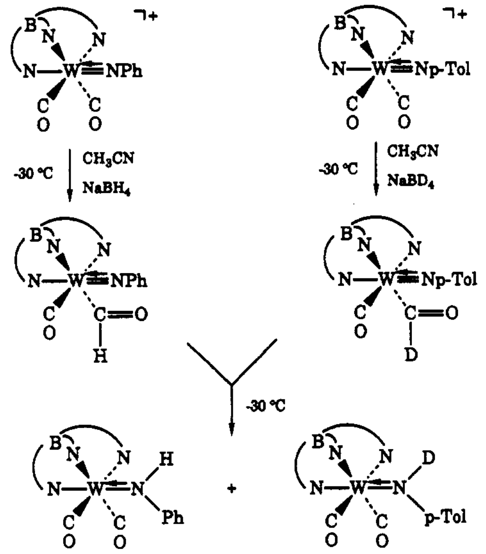


(3)

Scheme I



Scheme II



The formyl complex $Tp'W(CO)(NPh)(CHO)$ (1) is fluxional at low temperatures (eq 3). Three sharp ^{1}H NMR signals in a 1:1:1 ratio (C_1 symmetry) were observed for the pyrazole protons at −70 °C. As the sample is warmed, two of the three peaks begin to broaden and merge before coalescing at −41 °C. At the coalescence temperature the rate constant for site exchange is 40 s^{-1}, which corresponds to $\Delta G^{\ddagger}$ of 11.7 kcal/mol. We interpret these data as reflecting degenerate hydride migration from the formyl to the carbonyl ligand (eq 3).[7] Confirming that the fluxional process involves interconversion of the formyl and carbonyl carbons, the ^{13}C spectrum of the ^{13}C-enriched sample exhibits line broadening of the ^{13}CO and ^{13}CHO signals. At −50 °C in CD_3CN the width at half-height of each line is 10 Hz, corresponding to k = 25 s^{-1} and $\Delta G^{\ddagger}$ = 11.5 kcal/mol.[8] This value matches the one based on coalescence of the pyrazole ^{1}H signals.

Kinetic measurements by proton NMR spectroscopy at low temperatures established a first-order rate for the hydride migration from carbon to nitrogen (Scheme I).[7] We obtained data at −70 °C. The first-order rate constant for disappearance of the formyl 1 at −70 °C is $K_{obs} = 7.2 \times 10^{-6}$ s^{-1} with $\Delta G^{\ddagger}$ = 16.5 kcal/mol. Interconversion of the two amido isomers is known to be slow at these temperatures ($\Delta G^{\ddagger}$ > 20 kcal/mol)[1] so the ca. 1:1 ratio observed here represents the kinetically controlled ratio.

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[3] Acetonitrile is the best solvent for this reaction. Addition of methylene chloride (ca. 25%) still supports a clean reaction while lowering the freezing point and increasing the solubility of both the formyl and amido complexes.

[4] (a) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (b) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1 and references therein.

[5] An additional small peak observed at 14 ppm in the ^{1}H NMR spectrum may be the anionic bisformyl $Tp'W(CHO)_2(NPh)^-$, which is reminiscent of $CpRe(NO)(CHO)_2^-$ reported by Casey[4a] and Gladysz.[4b] We have no other evidence to support this hypothesis.

[6] Feng, S. G.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L.; Young, C. *Inorg. Chem.* **1991**, *30*, 2582.

[7] The precise mechanism of hydride transfer has not been established. Although we can not definitively rule out pathways involving initial hydride transfer to the metal, electron-counting guidelines require either dechelation of one arm of Tp′ or substantial bending of the nitrene ligand to accommodate metal hydride intermediates. Hence, we choose to discuss these transfer reactions in terms of simple migration from carbon to carbon or from carbon to nitrogen.

[8] The rate is calculated from the slow-exchange approximation $k = \pi[w_{1/2} - w_{1/2}(\text{natural})]$. The natural line width is based on the 2-Hz line width of $Tp'W(^*CO)_2(NHPh)$ which is present.

In order to determine if the hydride migration from carbon to nitrogen is intramolecular or intermolecular, crossover experiments were performed (Scheme II). Amido complex Tp′W(CO)$_2$[NH(*p*-Tol)] (4) and nitrene complex [Tp′W(CO)$_2$(N-*p*-Tol)][PF$_6$] (5) were synthesized according to the procedure we reported for the corresponding phenyl complexes.[1] The difference between the amido proton ^{1}H NMR signals for Tp′W(CO)$_2$(NHPh) and Tp′W(CO)$_2$[NH(*p*-Tol)] (4) of 0.04 ppm in CD$_2$Cl$_2$ is readily detectable at 400 MHz. The reactivity of the two nitrene complexes [Tp′W(CO)$_2$(N-*p*-Tol)][PF$_6$] (5) and [Tp′W(CO)$_2$(NPh)][PF$_6$] toward hydride reduction is essentially the same. Separate solutions of Tp′W(CO)(NPh)(CHO) and Tp′W(CO)(N-*p*-Tol)(CDO) were prepared[9] at low temperature. Half of each solution was mixed and allowed to react together at −30 °C for 4 h before room-temperature isolation prior to monitoring the ^{1}H NMR spectrum of the products. The control was provided by the unmixed solutions, which were also held at −30 °C for 4 h before room-temperature isolation. The low level of proton incorporation into the Tp′W(CO)$_2$(ND-*p*-Tol) product was the same in both the crossover and the control as anticipated for an intramolecular transfer of the hydride. The complementary experiments using Tp′W(CO)(NPh)(CDO) and Tp′W(CO)(N-*p*-Tol)(CHO) gave similar results.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM28938) and the Department of Energy (Grant DE-FG05-85ER13430) for financial support.

Registry No. 1, 139495-12-8; 3, 139495-13-9; [Tp′W(CO)$_2$(NPh)][PF$_6$], 129812-91-5; LiBH$_4$, 16949-15-8.

Supplementary Material Available: Text giving experimental details, including preparations and characterization data, for complexes 1–5 (4 pages). Ordering information is given on any current masthead page.

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[9] Lithium borohydride is the best hydride reagent among those we tested, but we used sodium borohydride here because the borodeuteride is readily available.

Kinetic Study of Isomerization Reactions of (Trimethylsilyl)methylsilylene-Bridged Diiron Complexes

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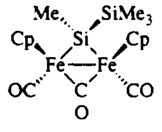
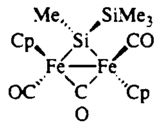
Summary: Kinetic study on the mutual isomerizations between three geometrical isomers of [CpFe(CO)]$_2$(μ-CO)(μ-SiMeSiMe$_3$) in C$_6$D$_6$ revealed that the reaction proceeds through the process cis(SiMe$_3$) $\rightleftarrows$ trans $\rightleftarrows$ cis(Me). A mechanism containing a silylene-bridged diiron complex with no Fe–Fe bond is proposed as the key intermediate for the isomerization reactions.

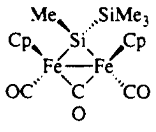
Recently, both Pannell's group[1] and our own[2] reported the study of the photolysis of the disilanylene-bridged diiron complex FpSiMe$_2$SiMe$_2$Fp (1; Fp = CpFe(CO)$_2$). During the early stages of the photolysis of 1 a mixture of a silylene-bridged diiron complex [CpFe(CO)]$_2$(μ-CO)(μ-SiMeSiMe$_3$) (2) and a bis(silylene)-bridged diiron complex [CpFe(CO)]$_2$(μ-SiMe$_2$)$_2$ (3) was formed, while, upon prolonged irradiation, 2 was quantitatively converted to 3.[2] During the course of the study, we found that, in solution, the silylene-bridged complex 2 exists as a mixture of all three possible geometrical isomers, cis(SiMe$_3$), cis(Me), and trans, which equilibrate in the ratio of 44.0:29.1:26.9, respectively, at 296 K in C$_6$D$_6$. We report here the kinetic study of the isomerization reactions of 2 in C$_6$D$_6$ and propose a possible mechanism for the reactions.



cis(SiMe$_3$)



trans



cis(Me)

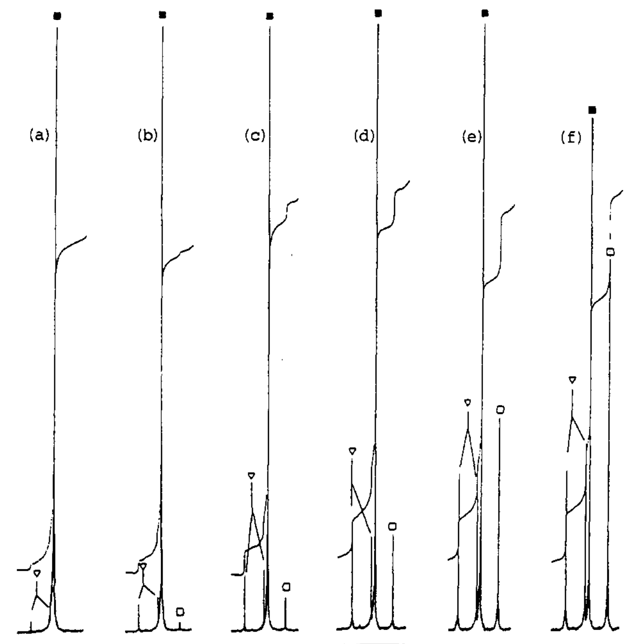


Figure 1. ^{1}H NMR spectral change of a C$_6$D$_6$ solution containing the cis(SiMe$_3$) isomer at 296 K at (a) 5 min, (b) 15 min, (c) 35 min, (d) 66 min, (e) 135 min, and (f) 415 min after dissolution. Key: ■, cis(SiMe$_3$); □, cis(Me); ▽, trans.

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[1] Pannell, K. H.; Sharma, H. *Organometallics* 1991, *10*, 954.

[2] Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* 1991, *10*, 959.

[3] Hoshino et al. also reported a useful method for computing the rate constants of a reversible, first-order, triangular network: Hoshino, Y.; Takahashi, R.; Shimizu, K.; Sato, G. P.; Aoki, K. *Bull. Chem. Soc. Jpn.* 1989, *62*, 993.

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