spectrum shows a singlet at δ 91.5, while the corresponding undecoupled spectrum shows a triplet with J_{PH} = 68 Hz. It is noteworthy that complexes **5** and **6** have been obtained in a spectroscopically pure form as established by Mössbauer spectrometry in the solid state and by NMR spectroscopy in solution. These results constitute direct evidence that the protonation of an M–H bond to give an η^2-H_2 complex is faster than the protonation of the same complex at the metal, as previously predicted.[14]

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Registry No. 1, 117696-31-8; 1-*d*, 132856-43-0; 2, 139524-38-2; 2-*d*, 139524-40-6; 2-*d*-CH_2Cl_2, 139524-41-7; 3, 139524-43-9; 4, 117696-30-7; 5, 139524-45-1; 5-*d*, 139524-47-3; 6, 139524-49-5.

Supplementary Material Available: A table of crystal data and data collection and refinement details and complete tables of atomic coordinates and their estimated standard deviations, bond lengths and angles, and general temperature factor expressions for 2 (12 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[14] (a) Heinekey, D. M.; Chinn, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Morris, R. H.; Jia, G. *J. Am. Chem. Soc.* **1991**, *113*, 875.

Structural and Spectroscopic Characterization of a Paramagnetic Isocyanide Complex of Rhodium(II)

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Summary: The remarkably stable paramagnetic Rh(II) complex $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) reacts with 2 equiv of *tert*-butyl isocyanide to yield the air-stable mononuclear Rh(II) complex $[Rh(\eta^3\text{-TMPP})_2(CNBu^t)_2][BF_4]_2$. A single-crystal X-ray diffraction study reveals that the cation adopts a distorted-square-planar geometry in which the phosphine ligands are trans rather than cis as in the parent complex. The paramagnetism of this unusual four-coordinate Rh(II) metallo radical was probed by a variety of spectroscopic and magnetic techniques.

The highly basic ether–phosphine ligand TMPP (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) forms unusual substitution products with a variety of transition-metal complexes, including those containing carbonyl, carboxylate, and acetonitrile ligands.[1] Of particular interest is the remarkable complex $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ (**1**), which represents the first mononuclear Rh(II) complex to be fully characterized by X-ray diffraction, magnetic susceptibility, and spectroscopic techniques.[2] Most of the documented research involving mononuclear rhodium complexes has focused on the +1 and +3 oxidation states, due, in large part, to their demonstrated involvement in homogeneous catalytic processes.[3] Only a limited number of reports have addressed the coordination chemistry of paramagnetic Rh(II),[4] and even fewer have focused on mononuclear organometallic complexes of Rh(II).[5] The unusual stability of **1** has presented us with a rare opportunity to investigate these elusive classes of compounds.[6] In light of the recent reports by Wayland and co-workers of carbon monoxide and methane activation by Rh(II) metallo radicals,[7] this is a particularly attractive area of research. We recently demonstrated that $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ reacts reversibly with CO through a pathway that involves the formation of Rh(I) carbonyl and Rh(III) intermediates.[8] Intrigued by this unusual chemistry, we set out to explore

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[†] Camille and Henry Dreyfus Teacher-Scholar, 1991–1995.

[1] (a) Dunbar, K. R.; Haefner, S. C.; Burzynski, D. J. *Organometallics* **1990**, *9*, 1347. (b) Chen, S. J.; Dunbar, K. R. *Inorg. Chem.* **1990**, *29*, 588. (c) Chen, S. J.; Dunbar, K. R. *Inorg. Chem.* **1991**, *30*, 2018.

[2] Dunbar, K. R.; Haefner, S. C.; Pence, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 5504.

[3] (a) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 5, p 228. (b) *Homogenous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983. (c) Parshall, G. W. *Homogenous Catalysis*; Wiley-Interscience: New York, 1980; p 89. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 523.

[4] (a) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73 and references therein. (b) Rawle, S. C.; Yagbasan, R.; Prout, K.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 6181. (c) Blake, A. J.; Gould, R. D.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1861. (d) Cooper, S. R.; Rawle, S. C.; Yagbasan, R.; Watkin, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 1600. (e) Pneumatikakis, G.; Psaroulis, P. *Inorg. Chim. Acta* **1980**, *46*, 97. (f) Pandey, K. K.; Nehete, D. T.; Sharma, R. B. *Polyhedron* **1990**, *9*, 2013. (g) Ogle, C. A.; Masterman, T. C.; Hubbard, J. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1733. (h) Anderson, J. E.; Gregor, T. P. *Inorg. Chem.* **1989**, *28*, 3905. (i) Bianchini, C.; Meli, A.; Laschi, F.; Vizza, F.; Zanello, P. *Inorg. Chem.* **1989**, *28*, 227.

[5] (a) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307. (b) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559. (c) Keller, H. J.; Wawersik, H. *J. Organomet. Chem.* **1967**, *8*, 185. (d) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (e) Dessy, R. E.; Kornmann, R.; Smith, C.; Hayter, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. (f) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660. (g) Bianchini, C.; Laschi, F.; Meli, A.; Peruzzini, M.; Zanello, P.; Frediani, P. *Organometallics* **1988**, *7*, 2575. (h) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893. (i) Pilloni, G.; Schiavon, G.; Zotti, L.; Zeechin, S. *J. Organomet. Chem.* **1977**, *134*, 305.

[6] (a) Vleck, A. *Inorg. Chim. Acta* **1980**, *43*, 35. (b) Holah, D. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* **1975**, *53*, 3669. (c) Valentini, G.; Braca, G.; Sbrana, G.; Colligiani, A. *Inorg. Chim. Acta* **1983**, *69*, 215. (d) Valentini, G.; Braca, G.; Sbrana, G.; Colligiani, A. *Inorg. Chim. Acta* **1983**, *69*, 221.

[7] (a) Wayland, B. B.; Sherry, A. E.; Coffin, V. L. *J. Chem. Soc., Chem. Commun.* **1989**, 662. (b) Wayland, B. B.; Sherry, A. E. *J. Am. Chem. Soc.* **1989**, *111*, 5010. (c) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259. (d) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.

[8] (a) Dunbar, K. R.; Haefner, S. C.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1991**, 460. (b) Haefner, S. C.; Dunbar, K. R.; Bender, C. *J. Am. Chem. Soc.* **1991**, *113*, 9540.

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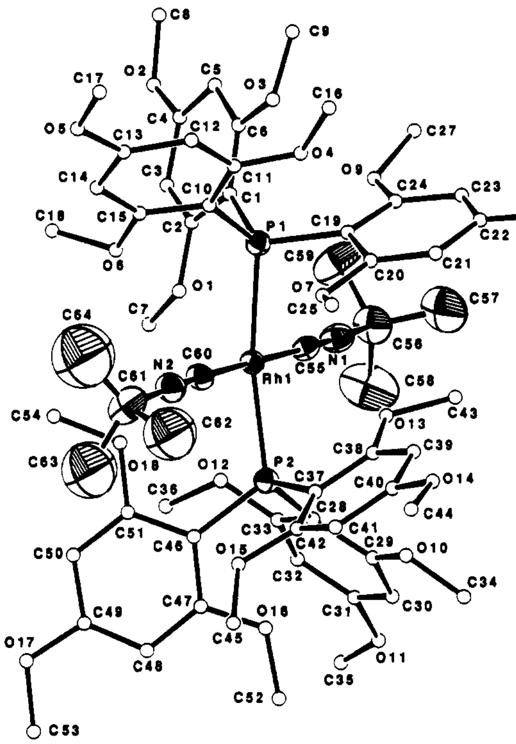

Figure 1. ORTEP representation of the molecular cation [Rh(TMPP)$_2$(CNBu^t)$_2$]$^{2+}$ in structure 3. Thermal ellipsoids are shown at the 40% probability level. Carbon and oxygen atoms of the phosphine ligand are shown as small spheres of arbitrary size for clarity. Selected bond distances (Å) and bond angles (deg) are as follows: Rh(1)–P(1), 2.364 (2); Rh(1)–P(2), 2.380 (2); Rh(1)–C(55), 1.990 (9); Rh(1)–C(60), 1.986 (8); C(55)–N(1), 1.16 (1); N(1)–C(56), 1.48 (1); P(1)–Rh(1)–P(2), 168.78 (8); P(1)–Rh(1)–C(55), 87.9 (2); P(1)–Rh(1)–C(60), 92.6 (2); C(55)–Rh(1)–C(60), 179.0 (3); Rh(1)–C(55)–N(1), 177.6 (7); C(55)–N(1)–C(56), 176.2 (9).

the reactivity of [Rh(η^3-TMPP)$_2$]$^{2+}$ with other π-acceptors such as NO, CN$^-$, PF$_3$, and CNR. We now wish to report the synthesis and full characterization of a novel square-planar Rh(II) complex stabilized by isocyanides and phosphines.

Dichloromethane solutions of [Rh(η^3-TMPP)$_2$][BF$_4$]$_2$ (1) react smoothly with 2 equiv of ^{t}BuNC to yield dark purple solutions that exhibit a characteristic ν(C≡N) band at 2200 cm^{-1}. Reactions with 1 equiv of ^{t}BuNC result in a 1:1 mixture of product and starting material, consistent with the formulation of the stable product as a bis adduct of 1. Concentration of the reaction solution followed by addition of THF produces a dark purple microcrystalline solid.[9] The product, [Rh(TMPP)$_2$(CNBu^t)$_2$][BF$_4$]$_2$ (2), was isolated in 90% yield and is remarkably air-stable both in the solid state and in solution.[10]

The identity of 2 as [Rh(TMPP)$_2$(CNBu^t)$_2$][BF$_4$]$_2$ was confirmed by an X-ray crystallographic study following general procedures described elsewhere.[11,12] Large single crystals of [Rh(TMPP)$_2$(CNBu^t)$_2$][BPh$_4$]$_2$ (3) were obtained by metathesis of [Rh(TMPP)$_2$(CNBu^t)$_2$][BF$_4$]$_2$ (2) with K[BPh$_4$] in acetone followed by slow diffusion of Et$_2$O.[13] An ORTEP drawing of the molecular cation [Rh(TMPP)$_2$(CNBu^t)$_2$]$^{2+}$ is shown in Figure 1. The cation contains mutually trans phosphine and isocyanide ligands arranged in a slightly distorted square plane, as evidenced by the angles C(55)–Rh(1)–C(60) = 179.0 (3)° and P(1)–Rh(1)–P(2) = 168.78 (8)°. Coordination of the *tert*-butyl isocyanide ligands has effected a cis-to-trans isomerization from 1 to 3 similar to that observed in the formation of [Rh(TMPP)$_2$(CO)$_2$][BF$_4$],[8] with one major exception; namely, the oxidation state has remained +2 in this case rather than reducing to +1 as in the CO compound. Unlike [Rh(η^3-TMPP)$_2$][BF$_4$]$_2$ (1), in which the rhodium atom is pseudooctahedral with two metal–phosphorus and four metal–ether interactions, the title compound is bound to TMPP only through the phosphorus lone pair, leading to a four-coordinate geometry. The shortest Rh–O distances along the axial direction in 3 are Rh(1)–O(1) = 2.851 (5) Å and Rh(1)–O(13) = 2.909 (6) Å; these are well outside the expected range for covalent bonding. The trans Rh–P bond distances of 2.364 (2) and 2.380 (2) Å are longer than those found in the parent Rh(II) complex and are indicative of the stronger trans effect exerted by the phosphine as compared to that of an ether donor.

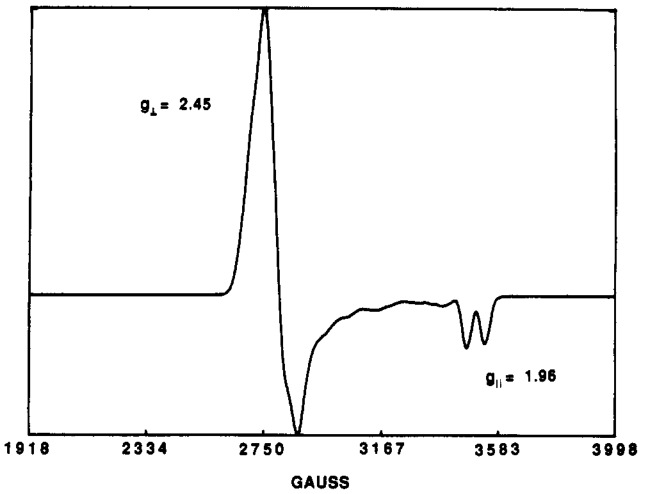

Figure 2. EPR spectrum of [Rh(TMPP)$_2$(CNBu^t)$_2$][BF$_4$]$_2$ (2) in the solid state at 100 K.

The paramagnetism of [Rh(TMPP)$_2$(CNBu^t)$_2$][BF$_4$]$_2$ (2) was probed by several spectroscopic and magnetic techniques. The ^{1}H and ^{31}P NMR spectra of 2 are broad and essentially featureless, consistent with the formulation of 2 as a paramagnetic species. The solid-state EPR spectrum of a polycrystalline sample of 2 at 100 K (Figure 2) shows an axial signal with $g_\perp = 2.45$ and $g_\parallel = 1.96$ with hyperfine coupling to ^{103}Rh ($I = {}^1/_2$) in the $g_\parallel$ region ($A_\parallel = 62$ G). The EPR spectrum in a 1:1 Me-THF/CH$_2$Cl$_2$ glass at 100 K exhibits a signal similar to that observed in the solid state ($g_\perp = 2.48$, $g_\parallel = 1.96$, $A_\parallel = 66$ G) with the exception that the $g_\perp$ region shows hyperfine coupling as well. A solid-state magnetic susceptibility measurement at 299 K led to a μ_{eff} value of 2.04 μ_B.[14] Solution susceptibility studies

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[9] Infrared data (Nujol mull, CsI, cm^{-1}): ν(C≡N), 2198 vs; other, 1595 vs, 1578 vs, 1411 s, 1332 s, 1294 w, 1228 s, 1207 s, 1185 w, 1160 s, 1122 s, 1087 s, 1054 s, 1026 s, 950 m, 917 m, 815 m, 675 w, 640 w, 536 w, 522 w, 479 m, 442 w.

[10] Anal. Calcd for C$_{64}$H$_{74}$F$_8$P$_2$O$_{18}$N$_2$B$_2$Rh: C, 50.98; H, 4.95. Found: C, 50.45; H, 5.88.

[11] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[12] Calculations were performed on a VAXSTATION 2000 computer using the TEXSAN Structure Analysis Package of Molecular Structure Corp.

[13] The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 26.810$ (7) Å, $b = 14.076$ (2) Å, $c = 27.809$ (6) Å, $\beta = 101.35$ (2)°, $V = 10289$ (4) Å^3, $Z = 4$, $d_{\mathrm{calc}} = 1.273$ g cm^{-3}, and μ(Mo Kα) = 2.57 cm^{-1}. A Rigaku AFC6S diffractometer was used to collect 14132 unique data in the range $4 \leq 2\theta \leq 47°$ at 23 ± 1 °C; 9109 data with $F_o^2 > 3\sigma(F_o^2)$ were used in refinement. Least-squares refinement of 1219 parameters gave residuals of $R = 0.056$ and $R_w = 0.071$. The quality-of-fit index was 3.80, and the largest shift/esd was 0.32.

[14] A diamagnetic correction of -880×10^{-6} cgsu was applied based on -24×10^{-6} cgsu for Rh^{2+}, -39×10^{-6} cgsu for [BF$_4$]$^-$, -330.8×10^{-6} cgsu for TMPP, and -58.5×10^{-6} cgsu for CNBu^t.

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.

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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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