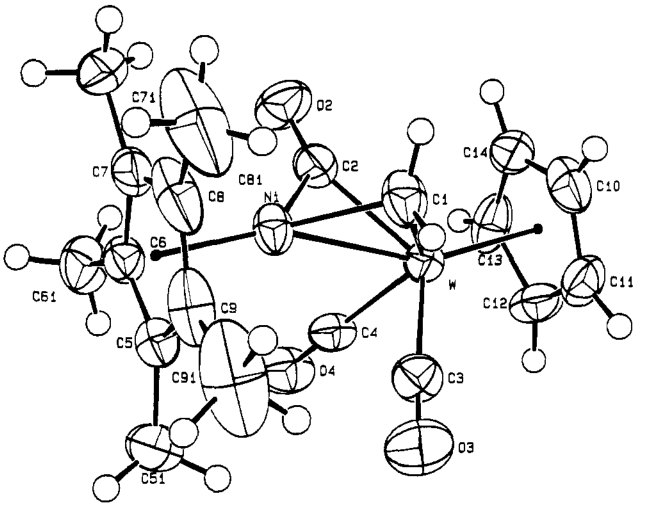
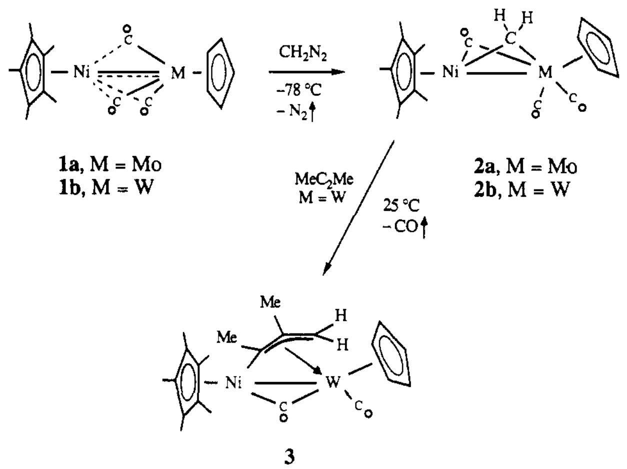


Figure 1. ORTEP diagram of $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CH_2)(\mu_2\text{-}CO)W(CO)_2(\eta^5\text{-}C_5H_5)$(*Ni–W*) (**2b**) (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ni–W = 2.5689 (6); Ni–C(1) = 1.906 (5); W–C(1) = 2.185 (5); Ni–C(2) = 1.916 (6); W–C(2) = 2.073 (6); Ni–C(1)–W = 77.5 (2); Ni–W–C(1) = 46.4 (1); Ni–C(2)–W = 80.1 (2); Ni–W–C(2) = 47.3 (1).

Scheme I. Reactions of 1a and 1b with Diazomethane and the Effective Insertion of MeC_2Me into the Ni–CH_2 Bond of 2b, Affording 3



Nickel and tungsten atoms are linked to $\eta^5\text{-}C_5Me_5$ and $\eta^5\text{-}C_5H_5$ groups respectively, and two terminal carbonyl ligands complete the tungsten atom's coordination sphere.

The CH_2 protons of **2b** (and **2a**) resonate as singlets in ^1H NMR spectra even at −70 °C, at variance with what is expected if the solid-state structure of **2b** is maintained in solution. However, ^{13}C NMR data establish the fluxionality of **2b**. At ambient temperatures a single broad CO signal is seen; at −40 °C it sharpens considerably and another CO resonance appears. A bridge–terminal carbonyl exchange process operative in **2b** may render the CH_2 protons equivalent.

Preliminary data indicate **2a** and **2b** are reactive species. Alkynes frequently insert into metal–carbon bonds of terminal or bridging alkylidene complexes, generally affording *vinyl carbene species or their derivatives.*[5a,20] **2b** forms $(\eta^5\text{-}C_5Me_5)Ni(\mu_2\text{-}CO)\{\mu_2\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}W(CO)(\eta^5\text{-}C_5H_5)$(*Ni–W*) (**3**) under very mild conditions when treated with 2-butyne. This species stems from the effective alkyne insertion into the nickel and not the tungsten–CH_2 bond of **2b** (Scheme I).[21] **3** is best regarded as a nickel-substituted π-allyl complex[22] in which the three allylic carbon atoms are coordinated to the tungsten atom. Its structure was deduced by the close correspondence of its spectral features[23] to those of the structurally characterized species $(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}CO)\{\mu_2\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}Mo(CO)(\eta^5\text{-}C_5H_4Me)$(*Ni–Mo*), which was prepared by a different synthetic route.[24] Further reactivity studies of **2a** and **2b** are underway.

Acknowledgment is made to the University of Notre Dame for financial assistance and to the National Science Foundation (Grant No. CHE 8615556) for the MICROVAX computer and Enraf-Nonius CAD 4 diffractometer.

Supplementary Material Available: Tables of crystal data and data collection parameters, atomic coordinates for non-hydrogen and hydrogen atoms, thermal parameters for non-hydrogen atoms, and bond lengths and angles of **2b** (10 pages); a structure factor listing (26 pages). Ordering information is given on any current masthead page.

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[20] For a recent example and list of leading references in this field, see: Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

[21] **2b** (161 mg, 0.298 mmol) was dissolved in hexane (15 mL), 2-butyne (32 μL, ~4 mmol) was added, and the solution was stirred overnight. The mixture was then filtered, concentrated, and cooled to −20 °C, affording crystals of **3** (85 mg, 50%). IR spectra of the mother liquor indicated that the main carbonyl-containing species present in solution was unreacted **2b**.

[22] The $C(Me)C(Me)CH_2$ fragment can bond in three electronically equivalent but structurally different $\mu\text{-}\eta^1,\eta^3$ modes in dimetal systems—as a vinyl carbene, as part of a dimetallacyclopentene species, or as a metal-substituted allyl. The structural characteristics of each class are outlined in a report of a similar diiron species: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803.

[23] Spectroscopic data for **3**: ^1H NMR (benzene-d_6) δ 4.29 (5 H, C_5H_5), 2.83 (d, H, CH*H*, J_{HH} = 2.1 Hz), 2.58 (d, H, C*H*H, J_{HH} = 2.1 Hz), 2.00 (3 H, Me), 1.85 (15 H, C_5Me_5), 1.56 (3 H, Me, J_{WH} = 3.6 Hz); ^{13}C NMR (benzene-d_6) δ 253.2 (μ-*C*O), 216.3 (*C*O), 125.2 (*C*Me), 100.2 (C_5Me_5), 98.2 (*C*Me), 90.1 (C_5H_5), 37.6 (CH_2), 27.2 (Me), 20.3 (Me), 9.4 (C_5Me_5); IR (ν(CO), hexane, cm^{-1}) 1930 (s), 1759 (μ-CO, s); MS (*m/e*, amu) 566 $(M)^+$, with the correct NiW isotopic envelope. Anal. Calcd for $NiWC_{23}H_{28}O_3$: C, 46.60; H, 4.98. Found: C, 46.85; H, 5.00.

[24] Chetcuti, M. J.; McDonald, S. R.; Rath, N. P. *Organometallics* **1989**, *8*, 2077.

Isolation and Structure of the Fluxional Phosphine Complex $(\eta^3\text{-}PR_3)Mo(CO)_3$ (R = 2,4,6-Trimethoxyphenyl)

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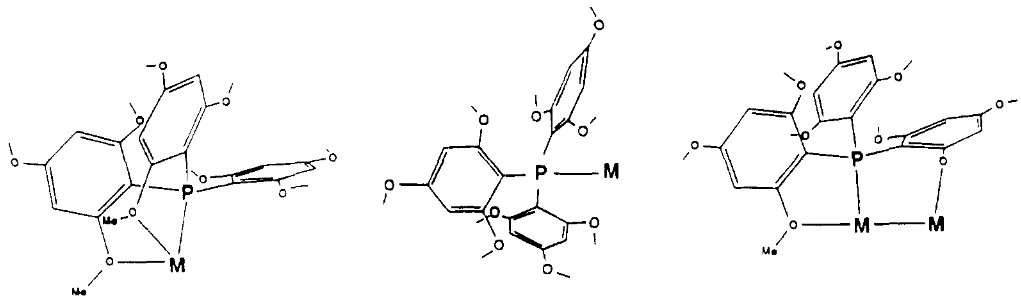
Summary: We report the synthesis of the novel fluxional molecule $(\eta^3\text{-}TMPP)Mo(CO)_3$ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) from a reaction between $(C_7H_8)Mo(CO)_3$ and TMPP. A single-crystal X-ray study revealed that the molecule is comprised of a Mo(0) center ligated by three carbonyl ligands and a TMPP ligand in a facial bonding mode. The metal–ether interactions from the pendant methoxy groups are quite labile. Variable-temperature ^1H NMR spectra in toluene-d_8 and CD_2Cl_2 reveal that a low-energy intramolecular exchange process is occurring.

We have been engaged in a broad study of the coordination chemistry of a versatile new phosphine ligand with transition metals possessing d^n configurations (n = 2–10). The tertiary phosphine ligand is tris(2,4,6-trimethoxy-

Chart I



a b c

phenyl)phosphine, which we will hereafter refer to as TMPP.[1] In addition to being quite bulky (cone angle 185°), TMPP is also unusually basic, as evidenced by its pK_a value of 11.0[1a] and the shift of ν(CO) bands in the infrared spectrum of $Ni(CO)_3(TMPP)$.[2] In size, TMPP is comparable to P-*t*-Bu_3[3] but its chemistry is expected to be significantly different, owing to the presence of the pendant methoxy groups. Indeed, we have demonstrated the novel ligation properties of TMPP by the preparation of the bis(phosphine) d^7 Rh(II) monomer $[Rh(TMPP)_2]^{2+}$.[1f,4] Other chemistry of $P[C_6(OMe)_3H_2]_3$ that is under investigation includes reactions with 3d transition-metal halides,[5] late-transition-metal cation complexes,[6] and M–M-bonded binuclear compounds.[7] The various binding modes for TMPP that have been exhibited in our chemistry to date are depicted in Chart I.

As our eventual goal in this research is to establish that TMPP, with its labile metal–ether interactions, is an excellent ligand for the design of reactive metal centers, we set out to prepare a complex that would allow us to probe the small-molecule binding properties of a TMPP-supported metal. On the basis of our newly acquired knowledge of the bonding capabilities of the ligand, we predicted that it would be possible to prepare compounds of general formula $(TMPP)ML_3$ for metals that ordinarily exhibit octahedral structures. A convenient backdrop for our work is the elegant research of Kubas and co-workers, who demonstrated that highly donating, bulky phosphine ligands stabilize the five-coordinate complexes $M(CO)_3(PR_3)_2$ (M = Mo, W; R = C_6H_{11}, *i*-C_3H_7), which readily add molecular H_2 and N_2.[8] Since no examples of four-coordinate complexes of general formula $M(CO)_3(PR_3)$ have been reported, we set out to prepare such a mono(phosphine) derivative with TMPP on the expectation that the product would exhibit unusual properties and reactivity.

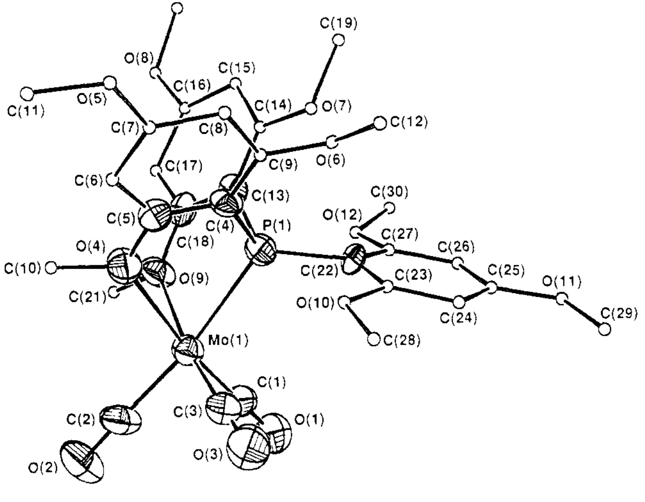


Figure 1. ORTEP representation of $Mo(CO)_3P[C_6(OMe)_3H_2]_3$. Some important distances (Å) and angles (deg) are as follows: Mo(1)–P(1), 2.476 (3); Mo(1)–C(1), 1.85 (1); Mo(1)–C(2), 1.97 (1); Mo(1)–C(3), 1.92 (1); Mo(1)–O(4), 2.363 (6); P(1)–Mo(1)–C(1), 101.3 (3); P(1)–Mo(1)–C(2), 171.5 (4); P(1)–Mo(1)–O(4), 71.6 (2); Mo(1)–P(1)–C(4), 104.8 (3); Mo(1)–P(1)–C(22), 120.8 (3).

One equivalent of $P[C_6(OMe)_3H_2]_3$ reacts smoothly with $(C_7H_8)Mo(CO)_3$ at room temperature in benzene over a period of 6 h to produce a yellow microcrystalline compound formulated as $Mo(CO)_3(TMPP)$ (**1**) in 80% yield.[9] The product is insoluble in most common solvents except toluene and benzene, in which it is sparingly soluble, and dichloromethane, in which it is very soluble but prone to decomposition over long periods of time. Yellow solutions of **1** are very air-sensitive, turning brown immediately upon exposure to air. The solid and crystalline forms decompose slowly over a period of several hours.

Single crystals of the title compound were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound at 0 °C.[10] An analysis of the X-ray data established the identity of the compound and revealed that the phosphine ligand occupies three positions in the coordination sphere of the molecule.[11] As the ORTEP diagram

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[1] (a) Wada, H.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482. (b) Wada, M.; Higashizaki, S.; Tsuboi, A. *J. Chem. Res., Synop.* **1985**, 38. (c) Wada, M. *Yuki Gosei Kagaku Kyokaishi* **1986**, 957. (d) Wada, M.; Tsuboi, A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 151. (e) Bowmaker, G. A.; Cotton, J. D.; Healy, P. C.; Kildea, J. D.; Silong, S. B.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1989**, *28*, 1462. (f) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 5504.

[2] The ν(CO) bands are 1963 (A_1) and 2048 (E) cm^{-1}. Dunbar, K. R.; Haefner, S. C., unpublished results.

[3] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[4] Dunbar, K. R.; Haefner, S. C.; Pence, L. E. Manuscript in preparation.

[5] Among the complexes that have been isolated are $FeCl_3(PR_3)$ and $FeCl_3(O{=}PR_3)$: Dunbar, K. R.; Haefner, S. C.; Quillevere, A. *Polyhedron*, in press.

[6] A monodentate mode for TMPP can be found in the d^{10} cation $Ag(TMPP)_2^+$ and in the d^8 complex $[Rh(TMPP)_2(CO)]^+$: Dunbar, K. R.; Haefner, S. C. Submitted for publication in *Inorg. Chem.*

[7] A bridging mode has been found for the TMPP ligand in $Rh_2(O_2CCH_3)_3(TMPP)(MeOH)$: Chen, S. J.; Dunbar, K. R. *Inorg. Chem.*, in press.

[8] (a) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61. (b) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (c) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (e) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (f) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (g) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17.

[9] Infrared data (ν(CO), cm^{-1}): Nujol, CsI, 1914 vs, 1775 vs, 1791 vs; CH_2Cl_2, 1921 vs, 1799 vs, 1782 vs; C_6H_6, 1930 vs, 1798 s.

[10] The compound $Mo(CO)_3(TMPP){\cdot}CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/a$ with a = 17.155 (8) Å, b = 12.019 (4) Å, c = 16.985 (6) Å, β = 95.69 (3)°, V = 3485 (2) Å^3, Z = 4, d_{calcd} = 1.493 g cm^{-3}, and μ(Mo Kα) = 6.22 cm^{-1}. A Nicolet P3/F diffractometer was used to collect 3845 unique data in the range $4 \leq 2\theta \leq 43°$ at 22 ± 2 °C; 2243 data with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Residuals of R = 0.069 and R_w = 0.084 were obtained. After 424 parameters had been refined to convergence, the quality-of-fit index was 2.09 and the largest shift/esd was 0.08.

[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.

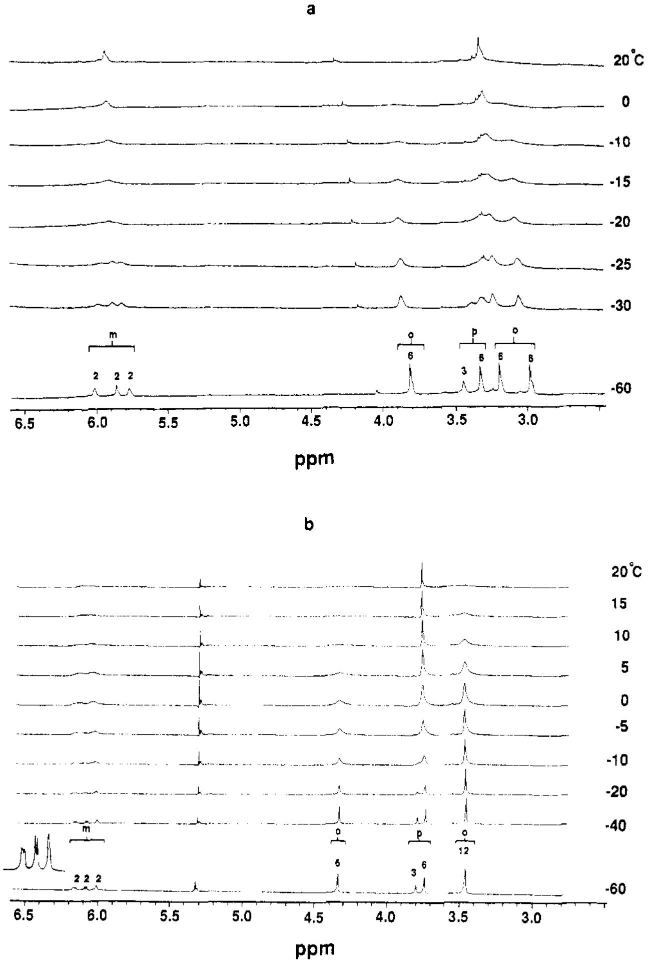

Figure 2. Variable-temperature ^1H NMR spectra of $Mo(CO)_3P[C_6(OMe)_3H_2]_3$ in (a) toluene-d_8 (500 MHz) and (b) CD_2Cl_2 (300 MHz; the signal at ~5.3 ppm is due to CD_2Cl_2 solvent impurity and interstitial CH_2Cl_2) (m = meta, o = ortho, p = para).

in Figure 1 shows, $Mo(CO)_3(TMPP)$ possesses a distorted-octahedral geometry with two of the coordination sites being occupied by oxygens from *o*-methoxy substituents on two separate phenyl rings. This bonding mode has previously been noted in the structure of $[Rh(TMPP)_2](BF_4)_2$.[1f] The chelation effect provided by weakly interacting pendant methoxy groups accounts for the ease of isolation and moderate stability of 1. The distortion of the coordination geometry about the Mo atom is evidenced most dramatically by the acute angles P(1)-Mo(1)-O of 71.6 (2) and 74.8 (2)° for O(4) and O(9), respectively. These deviations from 90° are a consequence of the formation of the five-membered rings Mo-P-C-C-O. All other angles within the molecule are also nonideal but to a lesser degree (see Figure 1 caption). The high degree of flexibility of the TMPP ligand in achieving the observed bonding mode is apparent from an examination of the disparate Mo(1)-P(1)-C angles; these vary from 104.8 (3)° for C(4), which is involved in a metallacycle, to 120.8 (3)° for C(22) on the lone free ring. Other metric parameters within the molecule are typical for carbonyl-phosphine complexes. The Mo-O distances of 2.363 (6) and 2.337 (7) Å are long, which is to be expected for metal-ether interactions. The Mo-C distances are inequivalent (see Figure 1 caption), with Mo-C(2) distance trans to the phosphorus being the longest (1.97 (1) Å).

The solution properties of $Mo(CO)_3(TMPP)$ attest to its high reactivity, as it easily converts to $Mo(CO)_3(NCCH_3)_3$ in acetonitrile and is extremely air-sensitive. The ^1H NMR spectrum of 1 revealed that an intramolecular exchange process involving the *o*-methoxy groups is occurring at room temperature. Variable-temperature ^1H NMR data were obtained in toluene-d_8 and CD_2Cl_2 over the range +20 to -60 °C, and the results clearly indicate that all three rings are participating in a low-energy fluxional process. The low-temperature limiting spectrum at -60 °C in toluene-d_8 (Figure 2) exhibits eight distinct resonances, which can be integrated in accordance with the magnetically inequivalent meta, ortho, and para groups observed in the solid-state structure.[12] Above -60 °C the spectral features broaden and gradually collapse in a nonsymmetrical manner due to a dynamic exchange of interacting and noninteracting *o*-methoxy groups. Concomitantly the para and meta regions broaden and eventually coalesce at ca. -15 °C. Similar behavior is observed in CD_2Cl_2, although in this solvent the low-temperature limiting spectrum shows only one broad resonance for the noninteracting *o*-methoxy groups at $\delta = +3.49$ ppm.[12] Attempts to obtain spectra at higher temperatures were thwarted by the thermal instability of the complex.

The title complex represents a unique phosphine derivative of molybdenum tricarbonyl. Our future interest in this molecule centers around its reactivity with small molecules. The solution lability of the metal-ether interactions is expected to provide the requisite open coordination sites for binding substrates.

Acknowledgment. We thank Dr. Gregory Kubas for helpful discussions and suggestions. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Michigan State University for financial support. X-ray equipment was supported by a grant from the National Science Foundation (Grant No. CHE-8403823).

Supplementary Material Available: Tables of crystallographic parameters, equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[12] (a) ^1H NMR (δ, toluene-d_8): *m*, 6.01, 5.86, 5.77; *o*, 3.81, 3.19, 2.80; *p*, 3.44, 3.33. (b) ^1H NMR (δ, CD_2Cl_2): *m*, 6.15, 6.07, 6.02; *o*, 4.36, 3.49; *p*, 3.82, 3.77.

Synthesis and Reactivity of Chiral Rhenium Amine and Amide Complexes of the Formulas $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHRR')]^+TfO^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$

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Summary: Reactions of racemic and optically active $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ with primary and secondary amines give the amine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHRR')]^+TfO^-$ with retention of configuration at rhenium. These react with *n*-BuLi to give amide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ that contain an unusually basic and nucleophilic nitrogen.