6110 *J. Am. Chem. Soc.* **1988**, *110*, 6110-6118

Divergent Kinetic and Thermodynamic Acidity in Organotransition-Metal Hydride Complexes: Synthesis, Structure, and Reactivity of the Rhenium Anion of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$

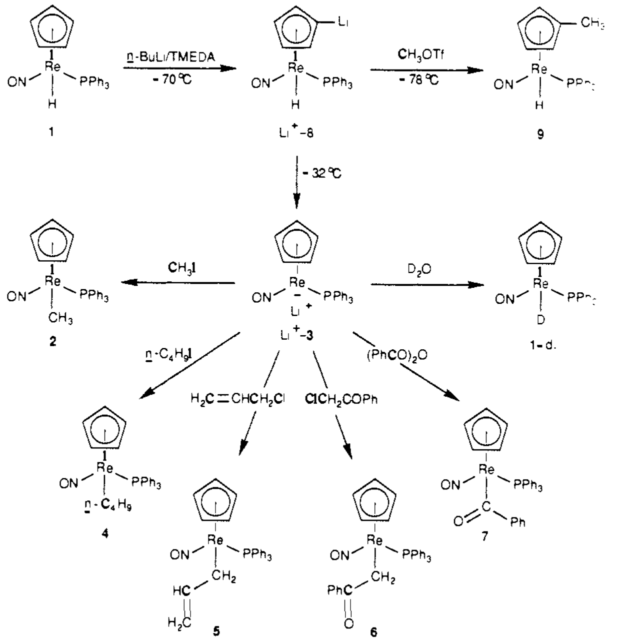
Guy L. Crocco and J. A. Gladysz*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received February 24, 1988*

Abstract: Reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**1**) and *n*-BuLi/TMEDA (THF, -78 °C) gives $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(H)$ (Li^+-**8**), as shown by ^{31}P NMR monitoring, deuterium labeling, and methylation ($CH_3OSO_2CF_3$, -78 °C) to $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(H)$ (**9**, 52%). Complex Li^+-**8** rearranges to the rhenium anion of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (Li^+-**3**; -32 °C, 0.5 h) with $\Delta H^{\ddagger} = 11.3 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -26.2 \pm 1.4$ eu, and k_H/k_D (-22.4 °C) $= 1.16 \pm 0.08$. Crossover experiments show hydrogen migration to be intramolecular, and K^+-**8** rearranges ca. 10^4 faster than Li^+-**8** at -91.6 °C. Equilibration experiments show the $\eta^5\text{-}C_5H_5$ and ReH proton pK_a's (THF) in **1** to be ca. 36 and 26-30, respectively. Thus, the less acidic proton is abstracted kinetically, and a rationale is proposed. Reactions of Li^+-**3** with alkylating agents (CH_3I, $n\text{-}C_4H_9I$, $ClCH_2CH{=}CH_2$, $ClCH_2COPh$), benzoic anhydride, and D_2O give the corresponding alkyl, acyl, and deuteride complexes (56-90%). IR data show Li^+-**3** to be a mixture of three ion pairs in THF. Pentamethyl analogue $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(H)$ (**13**) is prepared from methyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**11**; HCOOH, then 110 °C; 43%). Reaction of **13** and *n*-BuLi/K^+-*t*-BuO^- gives principally $K^+[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^-$, as assayed by ^{31}P NMR and methylation (CH_3I) to **11**.

Transition-metal hydride complexes are intermediates in virtually every metal-catalyzed reaction involving H_2.[1] As such, the chemical and physical properties of metal-hydrogen bonds are of great interest. Of these, acid/base properties are probably the most important and fundamental. However, whereas the thermodynamic and kinetic acidities of carbon-, nitrogen-, and oxygen-hydrogen bonds have been studied in great detail,[2,3] only recently have analogous investigations involving transition-metal hydride complexes begun to appear.[4-6]

Scheme I. Generation and Reactions of Rhenium Anion $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (Li^+-**3**).



Our interest in this subject was initiated by a simple synthetic objective. We have been conducting a detailed study of the chemistry of chiral rhenium complexes of the general formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$.[7] The d^6 pyramidal fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ is a strong π donor[7a,c,d,g,8] and stable complexes of a variety of unsaturated and saturated ligands have been synthesized. In order to extend our preparative capabilities, we sought a route to the d^8 "rhenium anion" $M^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$. This would be expected to be a very "electron rich" complex, and like other transition-metal anions it should readily react with a wide variety of electrophiles.[9]

Anionic transition-metal complexes are often synthesized, among other routes, by the deprotonation of metal hydride com-

---

(1) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: New York, 1981.

(2) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic: Orlando, FL, 1985.

(3) (a) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3447. (b) Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354. (c) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1. (d) Bernasconi, C. R. *Pure Appl. Chem.* **1982**, *54*, 2335.

(4) (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(5) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *198*, 403. (c) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (d) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *Ibid.* **1986**, *108*, 2257. (e) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *Ibid.* **1987**, *109*, 3945.

(6) (a) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (b) Hanckel, J. M.; Darensbourg, M. Y. *Ibid.* **1983**, *105*, 6979. (c) Gaus, P. L.; Kao, S. C.; Darensbourg, M. Y.; Arndt, L. W. *Ibid.* **1984**, *106*, 4752. (d) Darensbourg, M. Y.; Ludvig, M. M. *Inorg. Chem.* **1986**, *25*, 2894.

(7) See, inter alia: (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1983**, *2*, 5811. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103. (c) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837. (d) Bodner, G. S.; Patton, A. T.; Smith, D. E.; Georgiou, S.; Tam, W.; Wong, W.-K.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1987**, *6*, 1954. (e) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (f) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 37. (g) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

(8) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *Ibid.* **1979**, *101*, 592. (c) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109.

(9) (a) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. (b) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (c) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. L.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553. (d) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

0002-7863/88/1510-6110$01.50/0

plexes.[10] Hence, we undertook a study of the reactions of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**1**) with strong bases. As detailed below, the unusual acid/base chemistry observed prompted an extensive series of mechanistic experiments. The resulting body of data documents one of the few examples of divergent kinetic and thermodynamic acidity in organometallic compounds, and suggests structural features that may promote such behavior. A portion of this study has been communicated.[11]

Results

I. Generation and Reactions of the Rhenium Anion of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$. Hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**1**) was treated with n-BuLi/TMEDA (1.3 equiv)[12] in THF at −15 °C (10 min). Subsequent addition of CH_3I gave methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**)[13] in 72% yield after workup (Scheme I). In view of the abundant precedent for hydride ligand deprotonation noted above, this reaction was interpreted as proceeding via the rhenium anion of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (Li^+-**3**). Li^+-**3** was further characterized, and shown to be a versatile synthetic intermediate, by reactions with other electrophiles. Addition of $n\text{-}C_4H_9I$, $H_2C{=}CHCH_2Cl$, $ClCH_2COPh$, benzoic anhydride, and D_2O gave n-butyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(n\text{-}C_4H_9)$ (**4**, 66%), allyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CH_2)$ (**5**, 90%), "enolate" complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2COPh)$ (**6**, 56%), benzoyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COPh)$ (**7**, 68%),[14] and deuteride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(D)$ (**1**-d_1, 87%), respectively (Scheme I).

Similar yields were obtained when the above reactions were conducted without TMEDA. However, in some cases (reported elsewhere)[15] the absence of TMEDA facilitated workup. Small amounts (5–15%) of halide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$[16] formed in the reactions of Li^+-**3** with CH_3I, $H_2C{=}CHCH_2Cl$, and $ClCH_2COPh$, as assayed by ^{31}P NMR.[17] Reaction of Li^+-**3** with 2-iodobutane gave principally iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$.

New compounds were characterized by IR, mass, and ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Table I), and by microanalysis (Experimental Section). The IR ν_{ReH} of hydride complex **1** (1982 cm^{-1}) was a factor of 1.38 greater than the IR ν_{ReD} of deuteride complex **1**-d_1 (1433 cm^{-1}).[18] An analysis of the mass spectral fragmentation patterns has been reported elsewhere.[19]

II. Identification of the Kinetically Acidic Proton in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$. The spectroscopic detection of intermediates in the above transformations was attempted. The reaction of **1** with n-BuLi/TMEDA was monitored at −71 °C by ^{31}P NMR. Over the course of 1 h, **1** (28.2 ppm) disappeared as a new complex (Li^+-**8**, 33.9 ppm) appeared. The reaction was warmed to −32 °C. Over the course of 0.5 h, Li^+-**8** disappeared as another new complex (47.2 ppm) appeared. This species gave methyl complex **2** (25.4 ppm) upon addition of CH_3I, and was accordingly assigned as Li^+-**3**.

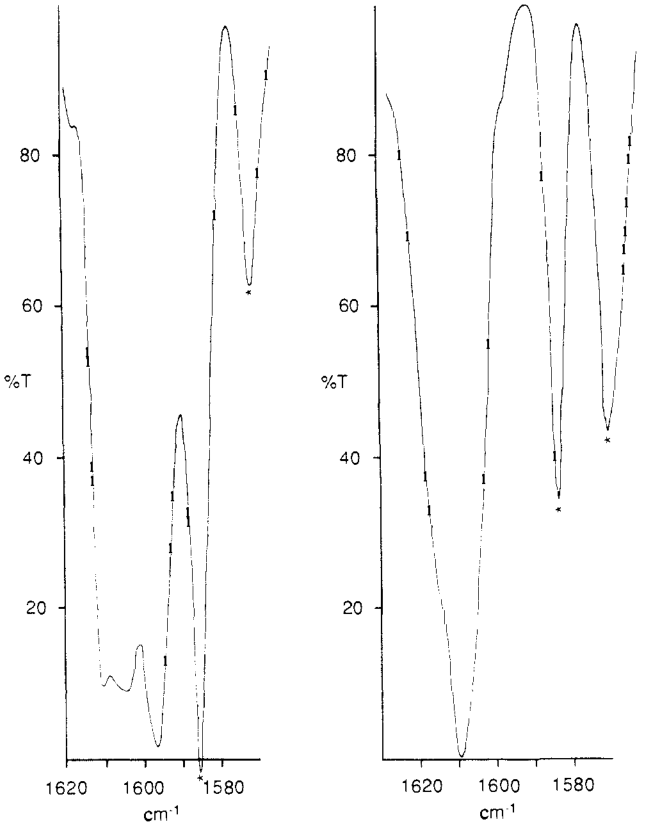


Figure 1. IR spectra of Li^+-**3** (left) and Li^+-**3**/12-crown-4 (right) in THF (−18 °C, cm^{-1}; an asterisk denotes peaks assigned to the PPh_3 ligand).

The trapping of intermediate Li^+-**8** was attempted. When CH_3OTf[12b] was added to Li^+-**8** at −49 °C, a new product (**9**, 29.1 ppm; ca. 80%)[17a] and minor amounts of **1** and **2** rapidly formed. Complex **9** was subsequently isolated in 52% yield. Its ^1H and ^{13}C NMR spectra (Table I) showed patterns characteristic of a monosubstituted cyclopentadienyl ligand.[20] A hydride ligand was evident in the ^1H NMR and IR spectra. Accordingly, **9** was assigned as methylcyclopentadienyl complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(H)$. The precursor Li^+-**8** was therefore assigned as lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(H)$. Hence, we conclude that the cyclopentadienyl ligand of **1**, rather than the hydride ligand, is initially deprotonated by n-BuLi/TMEDA.

Additional support for this conclusion was sought. Treatment of deuteride complex **1**-d_1 ((99 ± 1):(1 ± 1) d_1/d_0) with n-BuLi/TMEDA and CH_3I as above gave, as predicted from Scheme I, deuteriocyclopentadienyl complex $(\eta^5\text{-}C_5H_4D)Re(NO)(PPh_3)(CH_3)$ (**2**-d_1, (99 ± 1):(1 ± 1) d_1/d_0). Mass spectrometry indicated both the quantitative retention of deuterium and its presence in the cyclopentadienyl ligand. Similar treatment of *penta*deuteriocyclopentadienyl complex $(\eta^5\text{-}C_5D_5)Re(NO)(PPh_3)(H)$ (**1**-d_5, (90 ± 2):(10 ± 2) d_5/d_4) gave a (84 ± 2):(16 ± 2) mixture of *tetra*- and *penta*deuteriocyclopentadienyl complexes $(\eta^5\text{-}C_5D_4H)Re(NO)(PPh_3)(CH_3)$ (**2**-d_4) and $(\eta^5\text{-}C_5D_5)Re(NO)(PPh_3)(CH_3)$ (**2**-d_5). The minor pentadeuterio product

---

[10] This literature is extensive; selected references: (a) Muetterties, E. L.; Hirsekorn, F. J. *J. Chem. Soc., Chem. Commun.* **1973**, 683. (b) Kennedy, S.; Alexander, J. J.; Shore, S. G. *J. Organomet. Chem.* **1981**, *219*, 385. (c) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (d) Huffman, J. C.; Green, M. A.; Kaiser, S. L.; Caulton, K. G. *Ibid.* **1985**, *107*, 5111. (e) Bandy, J. A.; Berry, A.; Green, M. L. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1462.

[11] Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283.

[12] Abbreviations: (a) TMEDA = *N,N,N′,N′*-tetramethylethylenediamine. (b) OTf = OSO_2CF_3. (c) LDA = $Li^{+-}N(CH(CH_3)_2)_2$. (d) PMDT = 1,1,4,7,7-pentamethylethylenediamine.

[13] Tam, W.; Lin, G.-Y; Wong, W.-K; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

[14] Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

[15] Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics*, in press.

[16] Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

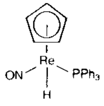
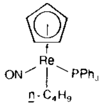
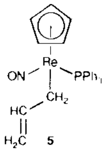
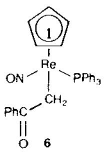
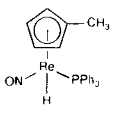
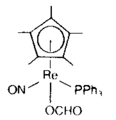
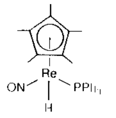
[17] (a) We have generally found product ratios determined from ^{31}P NMR spectra with a pulse delay of 1 s to be accurate to ±10%, as assayed by ^1H NMR integrations and quantitative ^{31}P NMR experiments. (b) For quantitative ^{31}P NMR data, spectra were recorded with gated decoupling and a pulse delay of $>10T_1$: Martin, M. L.; Delpuech, J.-J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: Philadelphia, 1980; p 362. (c) The following ^{31}P T_1 values were measured (s): **1**, 1.001; **2**, 0.603; Li^+-**3**, 0.380; **10**, 0.468.

[18] A factor of 1.41 is expected theoretically: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 97.

[19] Crocco, G. L.; Sharp, T. L.; Gladysz, J. A. *Int. J. Mass. Spectrom. Ion Phys.* **1986**, *73*, 181.

[20] (a) Johnston, P.; Loonat, M. S.; Ingham, W. L.; Carlton, L.; Coville, N. J. *Organometallics* **1987**, *6*, 2121. (b) Carlton, L.; Johnston, P.; Coville, N. J. *J. Organomet. Chem.* **1988**, *339*, 339.

Table I. Characterization of Rhenium Complexes

complex	IR (KBr, cm^{-1})	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (ppm)[b]	^{31}P{^{1}H} NMR (ppm)[c]	mass spectrum (m/e, ^{187}Re)
 1	$\nu_{N\equiv O}$ 1620 s ν_{Re-H} 1982 w	7.57–7.51 (m, 6 H of 3 C_6H_5); 7.07–6.97 (m, 9 H of 3 C_6H_5); 4.62 (s, C_5H_5); –9.15 (d, J_{HP} = 29.7, ReH)[d]	PC_6H_5 at 139.40 (d, J = 51.5, *ipso*), 134.08 (d, J = 11.0, *o*), 129.85 (s, *p*), 128.17 (*m*);[e] 85.25 (s, C_5H_5)[d]	28.22 (s)[d]	545 (M^+, 28%); 467 (M^+ – H – C_6H_5, 50%); 436 (M^+ – H – C_6H_5 – NO – H_2, 22%); 262 (PPh_3^+, 100%)[f]
 4	$\nu_{N\equiv O}$ 1620 s	7.58–7.51 (m, 6 H of 3 C_6H_5); 7.08–6.95 (m, 9 H of 3 C_6H_5); 4.60 (s, C_5H_5); 2.48 (m, 1 H); 2.08 (m, 3 H); 1.58 (m, 2 H); 1.09 (t, J = 7.4, CH_3)[d]	PC_6H_5 at 137.97 (d, J = 47.1, *ipso*), 134.38 (d, J = 10.9, *o*), 130.30 (s, *p*), 128.82 (*m*);[e] 89.72 (s, C_5H_5); alkyl carbons at 45.03 (s), 29.32 (s), 14.56 (s), –9.14 (d, J = 5.4, $ReCH_2$)[d]	26.05 (s)[d]	601 (M^+, 17%); 544 (M^+ – C_4H_9, 26%); 467 (M^+ – C_4H_9 – C_6H_5, 20%); 435 (M^+ – C_4H_9 – C_6H_5 – NO – H_2, 11%); 339 (M^+ – PPh_3, 5%); 262 (PPh_3^+, 100%)[g]
 5	$\nu_{N\equiv O}$ 1623 s $\nu_{C=C}$ 1607 m	7.48–7.32 (m, 3 C_6H_5); 6.22 (m, $ReCH_2CH$); 4.89 (s, C_5H_5); 4.37 (dd, J = 17.2, 2.6, $=CH_EH_Z$); 4.23 (dd, J = 10.1, 2.6, $=CH_EH_Z$); 2.78 (m, ReCHH′); 2.40 (ddd, J = 9.5, 9.5, 1.4 (HP), ReCHH′)[h]	153.20 (s, $ReCH_2CH$); PC_6H_5 at 136.91 (d, J = 51.4, *ipso*), 134.19 (d, J = 10.9, *o*), 130.60 (s, *p*), 128.88 (d, J = 10.7, *m*); 102.43 (s, $=CH_2$); 90.99 (s, C_5H_5); –5.75 (d, J = 5.2, $ReCH_2$)[h]	24.15 (s)[h]	585 (M^+, 6%); 544 (M^+ – C_3H_5, 2%); 323 (M^+ – PPh_3, 25%); 262 (PPh_3^+, 100%)[g]
 6	$\nu_{N\equiv O}$ 1623 s $\nu_{C=O}$ 1641 m	7.83–7.43 (m, 4 C_6H_5); 4.91 (s, C_5H_5); 3.62 (dd, J = 8.5, 6.7 (HP), ReCHH′); 2.91 (dd, J = 8.5, 3.9 (HP), ReCHH′)[i]	210.76 (d, J = 4.1, CO); CC_6H_5 at 139.73 (s, *ipso*), 131.29 (s), 128.30 (s), 128.24 (s); PC_6H_5 at 136.14 (d, J = 51.4, *ipso*), 133.99 (d, J = 9.5, *o*), 131.29 (s, *p*), 129.01 (d, J = 9.4, *m*); 91.58 (s, C_5H_5); 1.87 (s, $ReCH_2$)[i]	20.76 (s)[i]	663 (M^+, 7%); 544 (M^+ – CH_2COPh, 3%); 435 (M^+ – CH_2COPh – NO – C_6H_5 – H_2, 7%); 401 (M^+ – PPh_3, 17%); 262 (PPh_3^+, 100%)[g]
 9	$\nu_{N\equiv O}$ 1618 s ν_{Re-H} 1988 w	7.76–7.69 (m, 6 H of 3 C_6H_5); 7.08–6.95 (m, 9 H of 3 C_6H_5); C_5H_4 (br m) at 4.96, 4.49, 4.40, 4.29; 1.92 (s, CH_3); –8.79 (d, J_{HP} = 29.1, ReH)[d]	PC_6H_5 at 139.55 (d, J = 51.8, *ipso*), 134.13 (d, J = 11.2, *o*), 129.81 (s, *p*), 128.15 (*m*);[e] C_5H_4 (s) at 104.29 (*ipso*), 86.28, 85.30, 84.81, 83.23; 14.03 (s, CH_3)[d]	29.07 (s)[d]	559 (M^+, 2%); 481 (M^+ – H – C_6H_5, 2%); 278 (PPh_3O^+, 49%); 277 (PPh_3O^+ – H, 100%); 262 (PPh_3^+, 13%)[g]
 12	$\nu_{N\equiv O}$ 1657 s $\nu_{C=O}$ 1707 m	8.08 (d, J_{HP} = 0.8, ReOCHO); 7.65–7.58 (m, 6 H of 3 C_6H_5); 7.08–7.00 (m, 9 H of 3 C_6H_5); 4.36 (s, 0.5 CH_2Cl_2); 1.51 (d, J_{HP} = 0.6, $C_5(CH_3)_5$)[d]	169.95 (d, J = 5.5, CO); PC_6H_5 at 134.56 (d, J = 11.1, *o*), 134.53 (d, J = 48.3, *ipso*), 130.33 (s, *p*), 128.58 (d, J = 9.7, *m*); 100.41 (s, $C_5(CH_3)_5$); 53.40 (s, CH_2Cl_2); 9.99 (s, $C_5(CH_3)_5$)[d]	21.48 (s)[d]	615 (M^+ – CO_2, 4%); 537 (M^+ – OCHO – C_6H_5, 4%); 278 (PPh_3 – O^+, 27%); 277 (PPh_3O^+ – H, 35%); 262 (PPh_3^+, 75%); 134 ($C_5(CH_3)_5$ – H, 90%); 44 (CO_2^+, 100%)[f]
 13	$\nu_{N\equiv O}$ 1618 s ν_{Re-H} 1961 w	7.77–7.70 (m, 6 H of 3 C_6H_5); 7.06–6.97 (m, 9 H of 3 C_6H_5); 1.77 (s, $C_5(CH_3)_5$); –7.80 (d, J_{HP} = 31.8, ReH)[d]	PC_6H_5 at 139.05 (d, J = 48.7, *ipso*), 134.60 (d, J = 11.5, *o*), 129.80 (s, *p*), 128.39 (*m*);[e] 97.73 (d, J = 2.7, $C_5(CH_3)_5$); 11.36 (s, $C_5(CH_3)_5$)[d]	31.09 (s)[d]	615 (M^+, 86%); 614 (M^+ – H, 13%); 537 (M^+ – H – C_6H_5, 99%); 535 (M^+ – H – C_6H_5 – H_2, 40%); 400 (M^+ – H – C_6H_5 – H_2 – $C_5(CH_3)_5$, 23%); 262 (PPh_3^+, 100%)[g]

[a] At 300 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$; all couplings (Hz) are to hydrogen, unless noted. [b] At 75 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$; all couplings (Hz) are to phosphorus. Assignment of PPh_3 carbon resonances were made as described in ref 23. [c] At 32.2 MHz and ambient probe temperature and referenced to external 85% H_3PO_4. [d] Spectrum taken in C_6D_6. [e] Portion of doublet; other line obscured by solvent. [f] At 17 eV. [g] At 70 eV. [h] Spectrum taken in CD_2Cl_2. [i] Spectrum taken in $CDCl_3$. [j] Isolated as a 0.5 CH_2Cl_2 solvate.

Table II. Summary of IR ν_{NO} (THF, −18 °C) in $M^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (M^+-**3**).

compd	ν_{NO} (cm^{-1})
Li^+-**3**	1612 (s) 1607 (s) 1597 (s)
Li^+-**3**/12-crown-4	1610 (s)
K^+-**3**	1606 (s)
K^+-**3**/18-crown-6	1605 (s)

was not expected on the basis of Scheme I. Hence, the experiment was repeated with slightly better labeled **1**-d_5 ((94 ± 2):(6 ± 2) d_5/d_4) and monitored by ^{31}P NMR. Deprotonation of **1**-d_5 was only ca. 70% complete after 1.5 h at −49 °C, and some Li^+-**3**-d_x (ca. 20%) was present.[17a] The reaction was warmed to −15 °C and quenched with CH_3I. A (65 ± 2):(35 ± 2) **2**-d_4/**2**-d_5 mixture was obtained. Thus, as expected from the ^{31}P NMR data, *n*-BuLi/TMEDA abstracts a cyclopentadienyl proton of undeuteriated hydride complex **1**. However, substitution of the cyclopentadienyl ligand by a *pentadeuterio*cyclopentadienyl ligand renders, as a result of a kinetic isotope effect, direct hydride ligand deprotonation competitive.

III. Additional Syntheses and Properties of $M^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$. Further characterization of Li^+-**3** was sought. First, a low-temperature IR spectrum (−18 °C, THF, no TMEDA)[21] showed three IR ν_{NO} (Figure 1, Table II). The higher and lower frequency bands vanished upon addition of 12-crown-4, and the middle band shifted slightly in frequency. Subtraction of the PPh_3 ligand absorbances noted in Figure 1 did not reveal any additional absorbances. As expected, the ν_{NO} are lower than those found in neutral $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)$ complexes (1660–1620 cm^{-1}).

To facilitate acquisition of ^1H and ^{13}C NMR spectra, we sought to generate Li^+-**3** in the absence of the hexane solvent of commercial *n*-BuLi. Thus, hydride complex **1** was dissolved in THF-d_8 at −15 °C and treated with solid $Li^{+-}N(CH_3)_2$.[22] Li^+-**3** formed over the course of 3 h. The ^1H NMR spectrum (δ, −30 °C) showed resonances for $HN(CH_3)_2$ (2.54, s) and Li^+-**3** (7.79–7.74 (m, 6 H of $3C_6H_5$); 7.36–7.19 (m, 9 H of $3C_6H_5$); 3.60 (s, C_5H_5)). The ^{13}C NMR spectrum (ppm, −30 °C) showed $HN(CH_3)_2$ at 45.58 (br s) and Li^+-**3** at 143.50 (d, J_{CP} = 44.3 Hz, *ipso*), 135.14 (d, J_{CP} = 11.5 Hz, *o*), 128.61 (s, *p*), 127.29 (d, J_{CP} = 8.8 Hz, *m*),[23] and 69.74 (s, C_5H_5). The cyclopentadienyl ^1H and ^{13}C NMR resonances are much further upfield than those of cationic and neutral $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ complexes (*n* = 1: ^1H, 5.3–6.1 ppm; ^{13}C, 93–101 ppm; *n* = 0: ^1H, 4.5–5.5 ppm; ^{13}C, 88–95 ppm), evidencing a very electron rich metal center.

When deuteride complex **1**-d_1 ((99 ± 1):(1 ± 1) d_1/d_0) was treated with $Li^{+-}N(CH_3)_2$ as above and then CH_3I, deuteriocyclopentadienyl complex **2**-d_1 ((97 ± 2):(3 ± 2) d_1/d_0) was subsequently isolated. Hence, cyclopentadienyl ligand deprotonation is also preferred by weaker bases. Complex **1** and LDA[12] also reacted to give Li^+-**3** (1.0 h, −15 °C).

The generation of other complexes of formulae M^+-**8** and M^+-**3** was attempted. Treatment of **1**, with Schlosser base[24] *n*-BuLi/K^+-*t*-BuO^- at −98 °C rapidly (<5 min) gave, as assayed by ^{31}P NMR, potassiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4K)Re(NO)(PPh_3)(H)$ (K^+-**8**, 31.4 ppm). This species rearranged over the course of 0.5 h at −78 °C, a rate *much faster* than Li^+-**8**, to $K^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (K^+-**3**). K^+-**3** exhibited a *broad* ^{31}P NMR resonance (49–43 ppm), and it was then treated with CH_3I (−78 °C) to give a ca. 85:15 mixture of methyl complex **2** and iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$.[16,17a] When K^+-**3** was treated with 18-crown-6 (1.0 equiv, −50 °C, 45 min), the ^{31}P NMR resonance sharpened dramatically (44.0 ppm), and only **2** was obtained upon addition of CH_3I (−78 °C). Under all conditions, only one IR ν_{NO} was observed (Table II).

Table III. Summary of Hydride Ligand Migration Rates, M^+-**8** → M^+-**3**

entry	substrate	temp (°C)	10^4 *k* (s^{-1})
1	Li^+-**8**/TMEDA	−17.1	21.8 ± 2.4
2	Li^+-**8**/TMEDA	−22.4	15.4 ± 1.6
3	Li^+-**8**/TMEDA	−22.4	13.8 ± 1.6
4	Li^+-**8**/TMEDA	−23.9	13.2 ± 1.6
5	Li^+-**8**/TMEDA	−23.9	14.8 ± 1.6
6	Li^+-**8**/TMEDA	−29.8	6.20 ± 0.68
7	Li^+-**8**/TMEDA	−34.1	3.11 ± 0.34
8	Li^+-**8**/TMEDA	−36.2	2.68 ± 0.29
9	Li^+-**8**/TMEDA	−42.5	1.79 ± 0.20
10	Li^+-**8**/TMEDA	−43.8	1.91 ± 0.21
11	Li^+-**8**/TMEDA	−91.6	0.00143[a]
12	Li^+-**8**-d_1/TMEDA	−22.4	12.6 ± 4.4
13	Li^+-**8**-d_1/TMEDA	−22.3	13.4 ± 1.5
14	Li^+-**8**/no TMEDA	−22.4	11.3 ± 1.2
15	Li^+-**8**/no TMEDA	−22.5	12.1 ± 1.3
16	K^+-**8**	−91.6	12.0 ± 0.17
17	K^+-**8**	−91.6	10.3 ± 0.17

[a] Extrapolated value.

The isolation of Li^+-**3** and K^+-**3** was attempted. Complex Li^+-**3** was stable for 12 h at −15 °C, but decomposed over the course of 1 h at 0 °C. The solvent was removed from a solution of Li^+-**3** in vacuo at −15 °C. The residue was dissolved in THF at −15 °C, and a ^{31}P NMR spectrum showed a ca. 80:20 mixture of hydride complex **1** and Li^+-**3**. A sample of Li^+-**3**/12-crown-4 was layered with hexane at −78 °C. A red precipitate formed over the course of 6 days and was shown by ^{31}P NMR to be a ca. 45:55 mixture of **1** and Li^+-**3**/12-crown-4.

A sample of K^+-**3**/18-crown-6 was layered with hexane at −78 °C. A red precipitate formed over the course of 2 days and was shown by ^{31}P NMR to be a ca. 90:10 mixture of K^+-**3**/18-crown-6 (44.1 ppm) and **1** (28.0 ppm). Addition of CH_3I at −78 °C gave a (93 ± 2):(7 ± 2) mixture of methyl complex **2** and **1**, as assayed by ^1H NMR. The red solid could only be stored for short periods and immediately turned yellow on exposure to air. Additional attempts to isolate pure Li^+-**3** and K^+-**3** are described elsewhere.[25]

IV. Mechanism of Hydride Ligand Migration. The rate of the rearrangement Li^+-**8** → Li^+-**3** was measured by ^{31}P NMR under the conditions of Scheme I and over the temperatuure range −17.1 °C ($t_{1/2}$ = 5 min) to −43.8 °C ($t_{1/2}$ = 61 min). Rates were monitored through 2–3 half-lives and were first order in Li^+-**8**. The data, summarized in Table III, gave $\Delta H^\ddagger$ = 11.3 ± 0.5 kcal/mol, $\Delta S^\ddagger$ = −26.2 ± 1.4 eu, and $\Delta G^\ddagger_{298}$ = 19.1 ± 0.5 kcal/mol.[26] The rearrangement was slightly slower in the absence of TMEDA (Table III, entries 14 and 15) and exhibited a k_H/k_D (−22.4 °C) of 1.16 ± 0.08. The rate of the rearrangement K^+-**8** → K^+-**3** was measured at −91.6 °C (Table III, entries 16, 17), and was nearly 10^4 *faster* than the extrapolated rate of rearrangement of Li^+-**8** at −91.6 °C (entry 11).

A crossover experiment was conducted. A 1.00:0.94 mixture of **1** and pentadeuteriocyclopentadienyl deuteride complex $(\eta^5\text{-}C_5D_5)Re(NO)(PPh_3)(D)$ (**1**-d_6; (92 ± 2):(8 ± 2) d_6/d_5) was reacted with *n*-BuLi/TMEDA at −61 °C. This allowed the initial formation of Li^+-**8** (from **1**) and a substantial amount of Li^+-**8**-d_5 (from **1**-d_6, where a kinetic isotope is expected as with **1**-d_5 above). After 1 h, the mixture was warmed to −24 °C to initiate rearrangement (eq i). After an additional 1 h, CH_3I was added. This gave methyl complex **2** ((97 ± 2):(3 ± 2) d_0/d_1) and pentadeuteriocyclopentadienyl methyl complex $(\eta^5\text{-}C_5D_5)Re(NO)$-

---

[21] Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

[22] Chisholm. M. H.; Cotton, F. A.; Extine, M.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

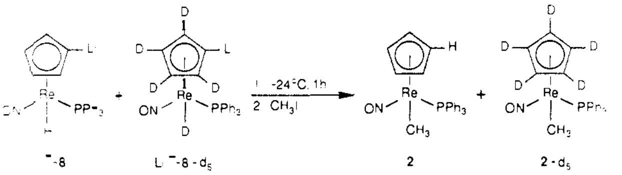
[23] Assignments of resonances to the PPh_3 carbons were made as follows. Both ipso and para (*p*) carbon resonances were easily distinguished on the basis of intensity and J_{PC}. The meta (*m*) resonance was assigned according to the proposal of Mann that it is the one closest to the chemical shift of benzene: Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

[24] This base has been shown to give alkyl potassium compounds: Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741 and references therein.

[25] Crocco, G. L. Ph.D. Dissertation, University of Utah, 1986.

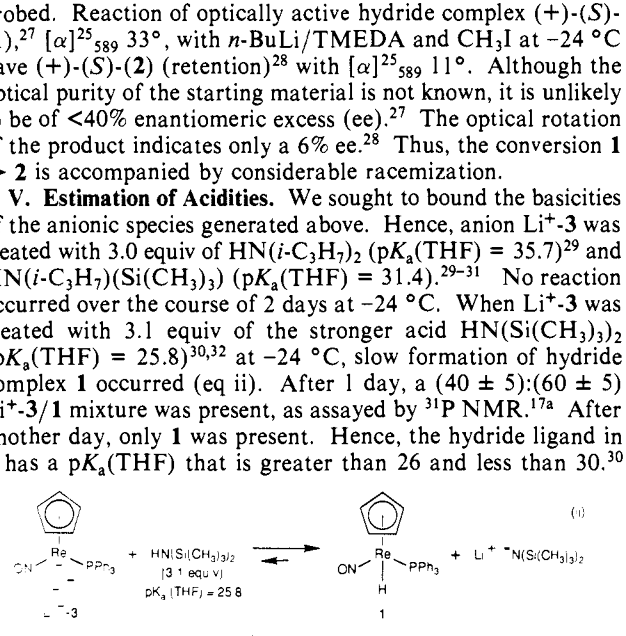
[26] Error limits were obtained by repeating rate measurements at a given temperature. The resulting error in *k* was propagated to the activation parameters. See: Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; Chapter 4.

(PPh$_3$)(CH$_3$) (**2**-d_5; (94 ± 2):(6 ± 2) d_5/d_4). Thus, hydride ligand migration is essentially intramolecular.

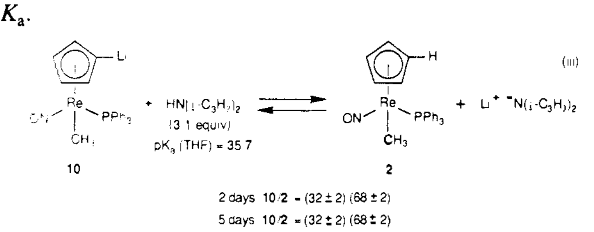


The stereochemistry of the rearrangement Li$^+$-**8** → Li$^+$-**3** was probed. Reaction of optically active hydride complex (+)-(*S*)-(**1**),[27] $[\alpha]^{25}_{589}$ 33°, with *n*-BuLi/TMEDA and CH$_3$I at -24 °C gave (+)-(*S*)-(**2**) (retention)[28] with $[\alpha]^{25}_{589}$ 11°. Although the optical purity of the starting material is not known, it is unlikely to be of <40% enantiomeric excess (ee).[27] The optical rotation of the product indicates only a 6% ee.[28] Thus, the conversion **1** → **2** is accompanied by considerable racemization.

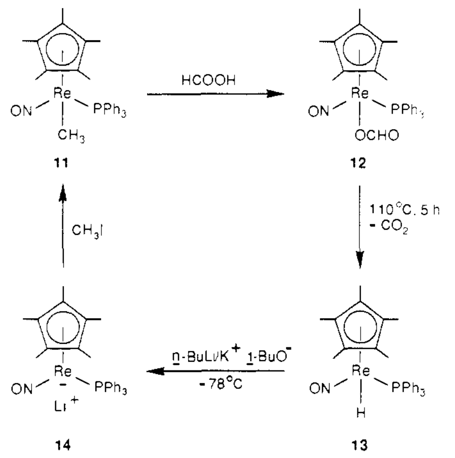
V. Estimation of Acidities. We sought to bound the basicities of the anionic species generated above. Hence, anion Li$^+$-**3** was treated with 3.0 equiv of HN(i-C$_3$H$_7$)$_2$ (pK_a(THF) = 35.7)[29] and HN(i-C$_3$H$_7$)(Si(CH$_3$)$_3$) (pK_a(THF) = 31.4).[29-31] No reaction occurred over the course of 2 days at -24 °C. When Li$^+$-**3** was treated with 3.1 equiv of the stronger acid HN(Si(CH$_3$)$_3$)$_2$ (pK_a(THF) = 25.8)[30,32] at -24 °C, slow formation of hydride complex **1** occurred (eq ii). After 1 day, a (40 ± 5):(60 ± 5) Li$^+$-**3**/**1** mixture was present, as assayed by ^{31}P NMR.[17a] After another day, only **1** was present. Hence, the hydride ligand in **1** has a pK_a(THF) that is greater than 26 and less than 30.[30]



Analogous experiments with lithiocyclopentadienyl hydride complex Li$^+$-**8** were hampered by its rapid rearrangement to Li$^+$-**3**. Hence, lithiocyclopentadienyl methyl complex (η^5-C$_5$H$_4$Li)Re(NO)(PPh$_3$)(CH$_3$) (**10**), which does not undergo methyl ligand migration,[33] was studied as a model. Both HN(Si(CH$_3$)$_3$)$_2$ (3.1 equiv, <5 min) and HN(i-C$_3$H$_7$)(Si(CH$_3$)$_3$) (3.0 equiv, 3 days) completely protonated **10** to methyl complex **2** in THF at -24 °C. The weaker acid HN(i-C$_3$H$_7$)$_2$ (3.0 equiv, 2 days, -24 °C) gave a mixture of **10** and **2** (eq iii). Quantitative ^{31}P NMR measurements[17b] indicated a (32 ± 2):(68 ± 2) **10**/**2** mixture. This ratio was unchanged after an additional 3 days. Hence, the cyclopentadienyl protons of **2** have a pK_a/hydrogen (THF) of 35.9.[34] The cyclopentadienyl protons of **1** should have a similar pK_a.



Scheme II. Synthesis and Deprotonation of Hydride Complex (η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(H) (**13**)



VI. Pentamethylcyclopentadienyl Complexes. Pentamethylcyclopentadienyl ligands are more electron releasing than cyclopentadienyl ligands[5d] and contain potentially acidic sp^3 carbon-hydrogen bonds. Hence, we sought to probe the acid/base chemistry of pentamethylcyclopentadienyl hydride complexes. First, the known pentamethylcyclopentadienyl methyl complex (η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(CH$_3$) (**11**; Scheme II)[35] was treated with formic acid. Workup gave formate complex (η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(OCHO) (**12**) in 88% yield. Complex **12** decarboxylated to hydride complex (η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(H) (**13**) in refluxing toluene. Workup gave **13** in 48% yield. This decarboxylation was much faster than that of cyclopentadienyl analogue (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(OCHO), consistent with the Re$^+$/$^-$OCHO ion pair mechanism proposed previously.[27]

Hydride complex **13** was treated with 1.2-10.0 equiv of *n*-BuLi/TMEDA at 0 °C. Over the course of 1.5-2.0 h, 10-25% conversion to a new anionic rhenium complex was observed by ^{31}P NMR (48.6-47.8 ppm). When **13** was treated with 1.6 equiv of *n*-BuLi/K$^+$-*t*-BuO$^-$ at -78 °C, very broad ^{31}P NMR resonances at 48-41 (ca. 75%) and 28-25 ppm (ca. 25%) rapidly appeared (<5 min). Subsequent addition of 18-crown-6 gave sharp resonances at 49.7 and 26.0 ppm. Addition of CH$_3$I then gave methyl complex **11** (25.8 ppm, ca. 75%) and three minor products (28.7 (ca. 25%), 27.2 (<5%), 14.7 (<5%) ppm). These were isolated in a combined yield of 87% but proved inseparable by silica gel HPLC or other chromatographic techniques. A ^{1}H NMR spectrum of the mixture confirmed **11** as the major product. From these data, the 49.7-ppm intermediate was assigned as the anion of K$^+$[(η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)]$^-$ (**14**). The minor 26.0-ppm resonance might possibily be due to the lithiated hydride complex (η^5-C$_5$Me$_4$CH$_2$Li)Re(NO)(PPh$_3$)(H).

Discussion

I. Structure and Reactivity of M$^+$[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$^-$. Scheme I establishes that Li$^+$-**3** readily metallates a variety of carbon electrophiles. Similar reactions of Li$^+$-**3** with silicon[15] and phosphorus[36] electrophiles have been described elsewhere. The formation of halide complex byproducts (η^5-C$_5$H$_5$)Re(NO)(PH$_3$)(X) suggests competing electron-transfer processes. Such behavior is well documented with other metal anions.[9d,37] Also, reactions of Li$^+$-**3** with certain types of electrophiles (e.g., acylating agents with enolizable protons) give substantial amounts of hydride complex **1**, as assayed in situ by ^{31}P NMR.

The solution structures of metal anions have frequently been probed by IR spectroscopy.[38-40] For example, Pannell and Jackson

---

(27) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782.

(28) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(29) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442.

(30) It should be emphasized that these pK_a values are more rigorously "ion pair acidities", since they are determined from equilibria between two acids and two (ion paired) conjugate bases, as opposed to a pure ionization.[31]

(31) (a) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Vol. 5A, pp 347-352. (b) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

(32) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

(33) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *106*, 1185.

(34) Statistical correction: pK_a/H = pK_a + log [(no. of equivalent ionizable hydrogens)/(no. of equivalent positions to which proton can return)].[31]

(35) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

(36) (a) Buhro, W. E. Ph.D. Dissertation, University of California, Los Angeles, 1985. (b) Zwick, B. D. Ph.D. Dissertation, University of Utah, 1987.

(37) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

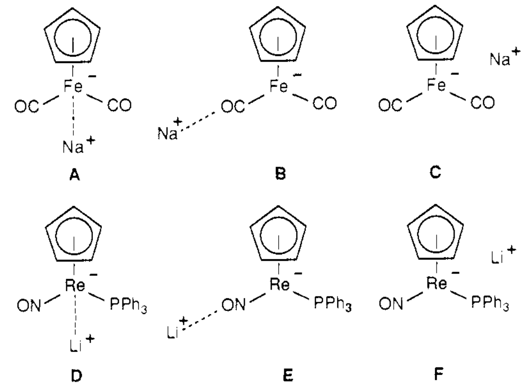


Figure 2. Established solution structures of Na$^+$[(η^5-C_5H_5)Fe(CO)$_2$]$^-$ (A–C)[38a] and proposed solution structures of Li$^+$[(η^5-C_5H_5)Re(NO)(PPh$_3$)]$^-$ (Li$^+$-3; D–F).

have shown that the iron carbonyl anion of Na$^+$[(η^5-C_5H_5)Fe(CO)$_2$]$^-$ (Figure 2) exists as a dynamic equilibrium of three distinct ion pairs in THF: **A** (ν_{CO} 1877, 1806 cm^{-1}; major), **B** (1862, 1770 cm^{-1}), and **C** (1862, 1786 cm^{-1}).[38a] Species **A** diminished upon addition of dibenzo-18-crown-6, while **B** and **C** increased. On the basis of the higher IR ν_{CO} of **A**, and other experiments, **A** was assigned as a Fe···Na$^+$ tight ion pair (Figure 2). Species **B** was shown to be a Fe—CO···Na$^+$ or Fe—CO···Na$^+$/18-crown-6 tight ion pair, consistent with its lower IR ν_{CO}. Species **C** was assigned as a solvent (or crown ether) separated ion pair. Nitay and Rosenblum found that THF solutions of lithium salt Li$^+$[(η^5-C_5H_5)Fe(CO)$_2$]$^-$ contain equal amounts of type-**A** and type-**B** ion pairs.[40] Metal nitrosyl anions such as those in Na$^+$[Fe(CO)$_3$(NO)]$^-$ have been shown to form M′"bdNO···M$^+$ tight ion pairs in THF.[38b]

The IR spectrum of Li$^+$-**3** in THF (Figure 1) similarly suggests the presence of three ion pairs: **D** (ν_{NO} 1612 cm^{-1}), **E** (1597 cm^{-1}), and **F** (1607 cm^{-1}). We propose that, by analogy to Pannell's study, (1) species **D**, which has the highest ν_{NO}, is a Re···Li$^+$ tight ion pair, (2) species **E**, which has the lowest ν_{NO}, is a Re—NO···Li$^+$ tight ion pair, and (3) species **F**, which has an intermediate ν_{NO}, is a solvent-separated ion pair. Accordingly, addition of 12-crown-4, which has a high binding constant for Li$^+$,[41] removes tight ion pairs **D** and **E** (Figure 1).[42]

Only a single IR ν_{NO}, identical with that of ion pair **F** above, is found for K$^+$-**3** in THF (1606 cm^{-1}). The IR spectrum is unaffected by the addition of 18-crown-6, which has a high binding constant for K$^+$.[41] Thus, we conclude that K$^+$-**3** is a solvent-separated ion pair in THF.

Another very important structural aspect of M$^+$-**3** is the geometry at rhenium. As can be rationalized from simple MO considerations, d^8 complexes of the formula (η^5-C_5H_5)MLL′ are expected to be "planar".[43] Hence, ion pairs **E** and **F** (Figure 2) should be achiral. This accounts for the formation of extensively racemized derivatives of Li$^+$-**3** when optically active hydride complex (+)-(*S*)-**1** is used in Scheme I. Finally, although we are unable to isolate a M$^+$-**3** species in pure form, crystal structures of a number of anionic metal complexes have been obtained.[10d,e,44] These structurally diverse compounds exhibit solid-state bonding between the alkali metal and various combinations of the transition metal, ancillary ligands, and donor solvents or additives.

II. Kinetic vs Thermodynamic Acidity in (η^5-C_5H_5)Re(NO)(PPh$_3$)(H) and Related Complexes. The above data clearly establish that the cyclopentadienyl protons of hydride complex **1** are kinetically the most acidic. The deprotonation of cyclopentadienyl ligands by strong bases has abundant precedent and has frequently been utilized in the preparation of functionalized cyclopentadienyl complexes.[45] However, few quantitative studies of such reactions have appeared. The pK_a of the cyclopentadienyl protons of iron complexes (η^5-C_5H_5)Fe(CO)$_2$(R) (R = C_6H_5, $CH_2C_6H_5$) has been estimated as 29–30 (ethanol/benzene) from rate data.[46] Note that two good π-accepting ligands (CO) are present on iron. The cyclopentadienyl protons of methyl complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$) (**2**), which has only one good π-accepting ligand, are less acidic (pK_a(THF) = 35.9; eq iii).

Quantitative aspects of metal hydride ligand acidity have been studied in much greater detail, particularly by Norton and coworkers.[5] Hydride ligand pK_a values vary over a wide range in both aqueous and nonaqueous solvents, and those of representative complexes HMn(CO)$_5$, HRe(CO)$_5$, and (η^5-C_5H_5)Fe(CO)$_2$H are (CH$_3$CN) 15.1, 21.2, and 19.4, respectively.[5d] The hydride ligand in **1** (pK_a(THF) 26–30) is one of the least acidic. This follows from the general periodic trend of lower acidity for third-row transition-metal hydrides,[5d] and the presence of only one good π-acceptor ligand on rhenium. Also, Bursten has advanced MO arguments to account for the low acidities of d^6 hydride complexes of formula (η^5-C_5H_5)MLL′H.[47] Finally, the replacement of cyclopentadienyl ligands by pentamethylcyclopentadienyl ligands in metal hydride complexes increases pK_a values (CH$_3$CN) by 3–7 units.[5d] Hence, hydride complex (η^5-C_5Me_5)Re(NO)(PPh$_3$)(H) (**13**, Scheme II) should have a pK_a(THF) of ≥30.

How is the more rapid abstraction of the less acidic cyclopentadienyl protons in **1** best accounted for? The PPh$_3$ ligand bulk might possibly retard the approach of base toward the hydride ligand. There is also a statistical factor due to the greater number of cyclopentadienyl protons. However, we suggest that the controlling factor is analogous to one often encountered in organic compounds. For carbon–hydrogen bonds of comparable pK_a, deprotonation to a resonance-stabilized carbanion is frequently slow relative to deprotonation to a localized carbanion.[3] Rehybridization and charge delocalization must occur in the former case, and hence the full thermodynamic stability of the carbanion is not reflected until later in the reaction coordinate. Similarly, *direct abstraction of the hydride ligand in* **1** *must be accompanied by rehybridization from an octahedral to a planar metal geometry.* No significant geometry changes occur upon cyclopentadienyl ligand deprotonation, so this process occurs more rapidly. Norton has previously emphasized the considerable structural changes that can occur upon metal hydride complex deprotonation and proposed this to contribute to slow *absolute* proton-transfer rates.[5b]

Hence, the reaction sequence **1** → M$^+$-**8** → M$^+$-**3** constitutes a new "ligand-assisted" mechanism for metal–hydride complex deprotonation. Literature data hint that other cyclopentadienyl metal hydride complexes are similarly deprotonated. For example, Stucky and Ephritikhine have reported that reactions of the *bent* hydride complex (η^5-C_5H_5)$_2$ReH (**15**, eq iv) with *n*-BuLi and then alkyl halides give alkyl complexes (η^5-C_5H_5)$_2$ReR (**16**).[48] Stucky

---

(38) (a) Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443. (b) Pannell, K. H.; Chen, Y.-S.; Belknap, K.; Wu, C. C.; Bernal, I.; Creswick, M. W.; Huang, H. N. *Inorg. Chem.* **1983**, *22*, 418.

(39) (a) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521. (b) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871. (c) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Ibid.* **1986**, *5*, 17.

(40) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23.

(41) Liotta, C. L. In *Synthetic Multidentate Macrocyclic Compounds*; Izatt, R. M., Christensen, J. J., Eds.; Academic: New York, 1978; pp 111–118.

(42) The IR ν_{NO} of Li$^+$-3/12-crown-4 shows a high-frequency shoulder (Figure 1). Pannell has observed similar ν_{NO} shoulders with several salts of iron anion [Fe(CO)$_3$(NO)]$^-$, and suggests that they arise from ion pair aggregates.[38b]

(43) (a) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536. (b) Albright, T.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 370–372. (c) Interestingly, MO considerations predict the d^6 cation [(η^5-C_5H_5)Re(NO)(PPh$_3$)]$^+$ to be pyramidal.

(44) (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 392. (b) Chan, A. S. C.; Shieh, H.-S. *J. Chem. Soc., Chem. Commun.* **1985**, 1379.

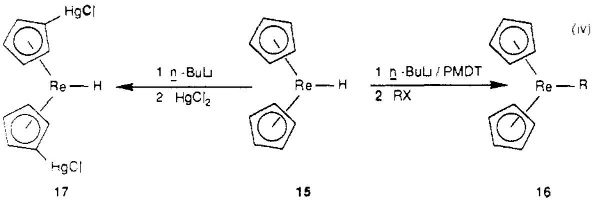
(45) (a) Nesmeyanov, A. N. *Adv. Organomet. Chem.* **1972**, *10*, 1. (b) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 910. (c) Crocco, G. L.; Gladysz, J. A. *Chem. Ber.* **1988**, *121*, 375.

(46) (a) Orlova, T. Y.; Setkina, V. N.; Sizoi, V. F.; Kursanov, D. N. *J. Organomet. Chem.* **1983**, *252*, 201. (b) Orlova, T. Y.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1984**, *267*, 309.

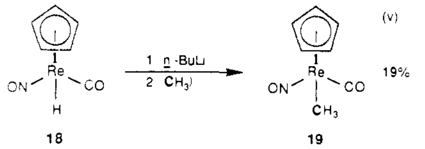
(47) (a) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554. (b) Bursten, B. E.; Gatter, M. G. *Organometallics* **1984**, *3*, 895, 941.

(48) (a) Mink, R. I.; Welter, J. J.; Young, P. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6928. (b) Baudry, D.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1979**, 895.

isolated the intermediate d^8 anion, Li^+/PMDT[12d] $[(\eta^5\text{-}C_5H_5)_2Re]^-$, which should have *parallel* cyclopentadienyl ligands as in isoelectronic group 8 metallocenes. However, Green found that reaction of $(\eta^5\text{-}C_5H_5)_2ReH$ with *n*-BuLi and then $HgCl_2$ gives **17** (eq iv), a product of cyclopentadienyl ligand deprotonation. Since direct deprotonation of the hydride ligand in **15** requires a considerable geometry change at rhenium, we suggest that the cyclopentadienyl ligand is initially deprotonated by alkyl lithium bases under all conditions.



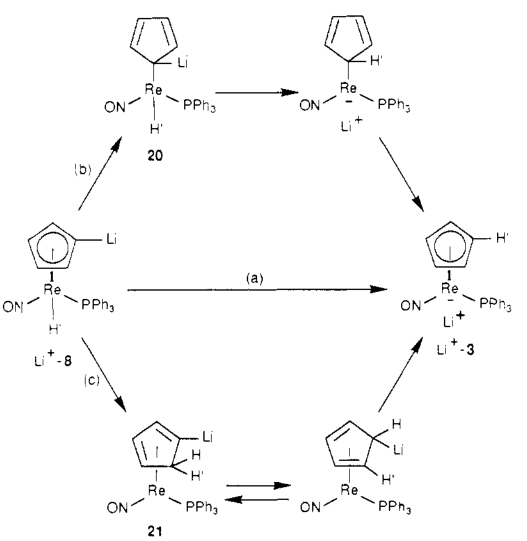
Dihydride complexes $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W) have been reported to deprotonate at the metal.[50] However, Norton found that reaction of dideuteride complex $(\eta^5\text{-}C_5H_5)_2WD_2$ with *n*-BuLi and then CH_3OTs gave methyl complex $(\eta^5\text{-}C_5H_5)_2W(H)(CH_3)\text{-}d_x$ in which the deuterium had been scrambled.[51] This might occur via cyclopentadienyl ligand deprotonation. Also, Russian researchers have reported that reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(H)$ (**18**, eq v) with *n*-BuLi and then CH_3I gives methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$.[52] However, experiments to define the initial site of deprotonation were not conducted.



How common will it be for metal hydride complexes to show contrasting kinetic and thermodynamic acidity? As noted above, hydride ligand deprotonation frequently entails a change of metal geometry. However, we speculate that Scheme I type behavior will be most probable with weakly acidic hydride complexes. In such cases, it is more likely that protons of comparable acidities will be found on ancillary ligands. Finally, consistent with the rehybridization/delocalization arguments given above, acyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2C_6H_5)$ also shows different kinetic and thermodynamic acidity.[33] The stronger amide base LDA[12c] (pK_{BH}(THF) = 35.7) rapidly deprotonates the cyclopentadienyl ligand at −78 °C, whereas the weaker base $Li^{+-}N(Si(CH_3)_3)_2$ (pK_{BH}(THF) = 25.8) slowly deprotonates the acyl ligand at 0 °C to a delocalized enolate ion.

III. Mechanism of Hydride Ligand Migration. We have previously generated a number of other lithiocyclopentadienyl complexes of the formula $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(X)$.[7b,15,33,45b,c] We find that acyl and silyl ligands, which have low-lying acceptor orbitals, rapidly migrate to give the corresponding rhenium anions $Li^+[(\eta^5\text{-}C_5H_4X)Re(NO)(PPh_3)]^-$ at −78 °C.[15,33] In general, ligands that lack low-lying acceptor orbitals (e.g., alkyl, halide, phosphido) show no tendency to migrate at 25 °C. However, the hydride ligand in Li^+-**8** exhibits an intermediate migratory aptitude, perhaps reflecting the intrinsic facility of prototropic rearrangments.

Scheme III. Three Possible Mechanisms for the Hydride Ligand Migration Li^+-**8** → Li^+-**3**.



We have also proposed the three general types of migration mechanisms shown in Scheme III:[33] (a) concerted migration, (b) initial $\eta^5\text{-}C_5H_4Li \rightarrow \eta^1\text{-}C_5H_4Li$ isomerization to give hydride complex **20**, followed by hydride ligand migration, and (c) initial hydride ligand migration to give η^4-cyclopentadiene complex **21**, followed by a 1,5-sigmatropic shift of the *exo* hydrogen. At present, we consider all of our data to be consistent with the simplest mechanism, concerted migration a. For example, the negative ΔS^{*} (−26.2 eu) indicates a highly ordered transition state. The primary kinetic deuterium isotope effect is low (1.16), but concerted hydride ligand migration clearly requires a nonlinear Re···H···C linkage in the transition state. Isotope effects in such situations are frequently close to unity.[53]

However, we are not yet able to rigorougly exclude ligand migration mechanisms b and c. We suggest that an electropositive substituent such as lithium should facilitate $\eta^5 \rightarrow \eta^1$ cyclopentadienyl ligand slippage, as the η^1 complex will have considerable aromatic cyclopentadienide $(Li^+(C_5H_4X)^-)$ character. Cyclopentadienyl ligand $\eta^5 \rightarrow \eta^1$ slippage has previously been proposed by Slocum and co-workers to account for facile base-catalyzed H/D exchange in substituted ferrocenes.[54] We have proposed an initial step analogous to that of mechanism c to account for scrambling of the deuteride ligand in **1**-d_1 into the cyclopentadienyl ligand at 80–100 °C.[27] However, it is not readily apparent why a cyclopentadienyl ligand lithium substituent should lower the temperature required for such a hydride migration by 100 °C, and why a potassium substituent should be still more effective. Thus, we view mechanism c as the least likely possibility in Scheme I.

The ca. 10^4 rate acceleration observed for M^+-**8** → M^+-**3** upon changing the cation from Li^+ to K^+ has precedent in anionic rearrangements of unsaturated organic alkoxides.[55] For example, Evans has shown that the rate of the oxy-Cope reaction (a [3.3]-sigmatropic shift) is dramatically increased as the alkoxide cation is varied in the order $Li^+ < Na^+ < K^+ < K^+$/18-crown-6.[55a] This trend, solvent effects, and other experiments show that solvent-separated ion pairs are the most reactive. Our IR data indicate that K_{eq} for solvent-separated ion pair formation increases upon going from Li^+-**3** to K^+-**3**. Although carbanions Li^+-**8** and K^+-**8** may be more tightly ion paired, the same trend should be followed. Hence, solutions of K^+-**8** should contain a higher concentration of the kinetically most reactive species.

IV. Summary. We have established a new "ligand assisted" mechanism for metal hydride complex deprotonation and analyzed

---

(49) Cooper, R. L.; Green, M. L. H.; Moelwyn-Hughes, J. T. *J. Organomet. Chem.* **1965**, *3*, 261.

(50) Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339.

(51) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.

(52) Labanova, I. A.; Zdanovich, V. J.; Kolobova, N. I. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* **1984**, *33*, 642.

(53) O'Ferrall, R. A. M. *J. Chem. Soc. B* **1970**, 785.

(54) Slocum, D. W.; Beach, D. L.; Ernst, C. R.; Fellows, R.; Moronski, M.; Conway, B.; Bencini, J.; Siegel, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1043.

(55) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Wilson, S. R.; Mao, D. T.; Jernberg, K. M.; Ezmirly, S. T. *Tetrahedron Lett.* **1977**, 2559. (c) Miyashi, T.; Hazato, A.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 1008. (d) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050.

structural features that can lead to divergent kinetic and thermodynamic acidity in such compounds. We predict that such phenomena, which are well documented in organic molecules, will not at all be uncommon in organometallic compounds. Further, recent studies indicate a variety of unusual rate effects in the deprotonation of metal hydride complexes.[6b,d] Finally, this study has shown the anion of M^+-**3** to be a useful synthetic reagent, and preparative applications will be reported in future publications.

Experimental Section

General. All reactions were conducted under a dry N_2 atmosphere. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. NMR spectra were recorded on Varian XL-300 (^1H, ^{13}C) and FT-80A (^{31}P) spectrometers as outlined in Table I. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Mass spectra were obtained on a VG 770 spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories.

Solvents were purified as follows: THF and benzene, distilled from Na/benzophenone; hexane, heptane, and toluene, distilled from Na; CH_2Cl_2, distilled from P_2O_5; acetone, distilled from $CaSO_4$; CH_3CN, distilled from CaH_2; ethyl acetate, used as received; $CDCl_3$, vacuum transferred from P_2O_5; C_6D_6, CD_2Cl_2, and THF-d_8, vacuum transferred from CaH_2.

Bases were obtained as follows: *n*-BuLi (Aldrich), standardized[56] before use; LDA, prepared from *n*-BuLi and $HN(CH(CH_3)_2)_2$ in hexane[57] and standardized[58] before use; $Li^{+}\,{}^{-}N(CH_3)_2$, prepared from *n*-BuLi and $HN(CH_3)_2$;[22] K^+-*t*-BuO^- (Aldrich), sublimed twice before use; $HN(CH(CH_3)_2)_2$ (Aldrich), TMEDA (Aldrich), and $HN(Si(CH_3)_3)_2$ (Petrarch), distilled from CaH_2; anhydrous $HN(CH_3)_2$ gas (Fluka), used as received.

Reagents were purified as follows: CH_3I (Aldrich), distilled from P_2O_5 and stored over Cu; $CH_3OSO_2CF_3$ (Aldrich), distilled from CaH_2; *n*-C_4H_9I (Aldrich), distilled from $MgSO_4$; $CH_2{=}CHCH_2Cl$ (Kodak), distilled from $CaCl_2$; $(C_6H_5CO)_2O$ (Sigma), dissolved in benzene, washed with $NaHCO_3$, and recrystallized from benzene/hexane; $ClCH_2COPh$ (Aldrich), recrystallized from ethanol; D_2O (Stohler), 88% aqueous HCOOH (Fisher), and $LiAlD_4$ (Aldrich), used as received; 12-crown-4 (Alfa), distilled from Na; 18-crown-6 (Aldrich), recrystallized from CH_3CN.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (1). This procedure is based upon syntheses described earlier by Merrifield.[16,27,59] A Schlenk flask was charged with **2** (2.1 g, 3.8 mmol),[13] CH_2Cl_2 (100 mL), and a stir bar. Then 88% aqueous HCOOH (1.0 mL, 1.2 g, 25 mmol) was added with stirring. After 12 h, solvents were removed by rotary evaporation. The residue was extracted with CH_2Cl_2. The extract was filtered through a 1-cm silica gel plug with 10:90 (v/v) acetone/CH_2Cl_2. Solvent was removed from the filtrate by rotary evaporation, and the resulting red gum was dissolved in toluene (100 mL) and transferred to a flask equipped with a reflux condenser. The solution was refluxed for 1–2 days, and the toluene was removed by rotary evaporation. The resulting yellow solid was dissolved in CH_2Cl_2 (ca. 100 mL). The solution was concentrated to ca. 40 mL and chromatographed on a 28 × 2.5 cm silica gel column with 50:50 (v/v) CH_2Cl_2/hexane. A broad orange band was collected and concentrated to ca. 20 mL. Small orange crystals formed, which were collected by filtration and dried in vacuo to give **1** (2.3 g, 4.2 mmol, 90%), mp 182–183 °C dec (lit.[13] mp 183–186 °C dec). A ^1H NMR spectrum was identical with that of an authentic sample.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (2). A Schlenk tube was charged with **1** (0.11 g, 0.21 mmol), THF (5 mL), and a stir bar. The yellow solution was cooled to −15 °C and stirred. Then TMEDA (0.031 g, 0.26 mmol) and *n*-BuLi (0.14 mL, 2.0 M in hexane) were added, and the solution turned dark red. After 0.5 h, CH_3I (0.068 g, 0.48 mmol) was added. After 5 min, the resulting light orange solution was transferred to a round-bottom flask, and the solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered and solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was chromatographed on a 28 × 2.5 cm silica gel column with 10:90 (v/v) ethyl acetate/hexane. The orange band was collected, concentrated to an orange powder by rotary evaporation, and dried in vacuo to give **2** (0.089 g, 0.16 mmol. 76%), mp 196–197 °C (lit.[13] mp 198–200 °C). A ^1H NMR spectrum was identical with that of an authentic sample of **2**.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(n\text{-}C_4H_9)$ (4). Complex **1** (0.20 g, 0.38 mmol), THF (10 mL), TMEDA (0.050 g, 0.45 mmol), and *n*-BuLi (0.19 mL, 2.5 M in hexane) were combined as described in the preparation of **2**, and after 0.5 h the dark red solution was cooled to −78 °C. Then *n*-C_4H_9I (0.15 g, 0.80 mmol) was added. After 5 min, the resulting light orange solution was transferred to a round-bottom flask, and solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered through a 2-cm silica gel plug, and the filtrate was concentrated to an orange oil by rotary evaporation. The oil was dissolved in hexane (50 mL). This solution was concentrated to ca. 20 mL and was kept at −25 °C for 4 days. The resulting red-orange crystals were collected by filtration and dried in vacuo at 57 °C to give **4** (0.15 g, 0.25 mmol, 66%), mp 168–170 °C. Anal. Calcd for $C_{27}H_{29}NOPRe$: C, 53.99; H, 4.87. Found: C, 53.97; H, 4.86.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CH_2)$ (5). Complex **1** (0.15 g, 0.28 mmol), THF (8 mL), TMEDA (0.038 g, 0.33 mmol), and *n*-BuLi (0.20 mL, 2.0 M in hexane) were combined as described in the preparation of **4**. Then $CH_2{=}CHCH_2Cl$ (0.066 g, 0.86 mmol) was added (−78 °C). After 5 min, the solution was warmed to room temperature and solvents were removed in vacuo. The flask was transferred to a glovebox and the orange oil was extracted with benzene. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting oil was dissolved in toluene (5 mL), layered with heptane, and kept at −40 °C for 2 days. The resulting small orange crystals were collected by filtration and dried in vacuo to give **5** (0.15 g, 0.25 mmol, 90%), mp 147–149 °C. Anal. Calcd for $C_{26}H_{25}NOPRe$: C, 53.40; H, 4.32. Found: C, 53.11; H, 4.42.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COPh)$ (7). Complex **1** (0.10 g, 0.19 mmol), THF (5 mL), TMEDA (0.027 g, 0.23 mmol), and *n*-BuLi (0.12 mL, 2.0 M in hexane) were combined as described in the preparation of **2**. Then $(PhCO)_2O$ (0.065 g, 0.29 mmol) was added (−15 °C). After 1 h, the reaction was worked up as described for **2** (chromatography with 30:70 (v/v) acetone/hexane). This gave **7** as a yellow-orange powder (0.084 g, 0.13 mmol, 68%), mp 198–200 °C dec (lit.[14] mp 198–202 °C dec). A ^1H NMR spectrum was identical with that of an authentic sample of **7**.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2COPh)$ (6). Complex **1** (0.22 g, 0.41 mmol), THF (12 mL), TMEDA (0.055 g, 0.50 mmol), and *n*-BuLi (0.21 mL, 2.5 M in hexane) were combined as described in the preparation of **4**. Then $ClCH_2COPh$ (0.13 g, 0.85 mmol) was added (−78 °C). After 0.5 h, the resulting orange solution was transferred to a round-bottom flask and the solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered and solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was chromatographed on a 28 × 2.5 cm silica gel column with 20:80 (v/v) ethyl acetate/hexane. The orange band was collected and concentrated to an oil by rotary evaporation. The oil was dissolved in CH_2Cl_2 (10 mL), layered with hexane, and kept at −25 °C for 2 days. The resulting small orange crystals were collected by filtration and dried in vacuo at 57 °C to give **6** (0.15 g, 0.23 mmol, 56%), mp 199–201 °C dec. Anal. Calcd for $C_{30}H_{28}NO_2PRe$: C, 55.28; H, 4.33. Found: C, 55.23; H, 4.11.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(D)$ (1-d_1). Complex **1** (0.11 g, 0.21 mmol), THF (5 mL), TMEDA (0.031 g, 0.26 mmol), and *n*-BuLi (0.15 mL, 2.0 M in hexane) were combined as described in the preparation of **2**. Then D_2O (0.015 g, 0.75 mmol) was added (−15 °C). After 15 min, the solution was transferred to a round-bottom flask, and solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting yellow oil was dissolved in CH_2Cl_2 (10 mL) and hexane (30 mL) was added. This solution was concentrated to ca. 10 mL by rotary evaporation. This gave a yellow-orange precipitate, which was collected by filtration and dried in vacuo to give **1**-d_1 (0.10 g, 0.19 mmol, 91%). IR (cm^{-1}, KBr): $\nu_{N{=}O}$ 1624 s, ν_{Re-D} 1433 w.

Preparation of $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(H)$ (9). Complex **1** (0.10 g, 0.19 mmol), THF (5 mL), TMEDA (0.029 g, 0.25 mmol), and *n*-BuLi (0.13 mL, 2.0 M in hexane) were combined at −49 °C as described in the preparation of **2**. After 1 h, $CH_3OSO_2CF_3$ (0.10 g, 0.61 mmol) was added (−49 °C). After 0.5 h, the solution was transferred to a round-bottom flask, and solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered through a 2-cm silica gel plug, and solvent was removed from the filtrate by rotary evaporation. The resulting oil was chromatographed on a preparative silica gel LC column with 10:90 (v/v) ethyl acetate/hexane. The major component was collected, concentrated to a yellow powder by rotary evaporation, and dried in vacuo to give **9** (0.055 g, 0.099 mmol, 52%), mp 120–121 °C dec. Anal. Calcd for $C_{24}H_{23}NOPRe$: C, 51.59;

---

(56) Silveira, A., Jr.; Bretherick, H. D., Jr.; Negishi, E. *J. Chem. Educ.* **1979**, *56*, 560.

(57) House, H. O.; Phillips, W. V.; Sayer, T. S. B.; Yau, C.-C. *J. Org. Chem.* **1978**, *43*, 700.

(58) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

(59) Merrifield, J. H. Ph.D. Dissertation, University of California, Los Angeles, 1983.

H, 4.16. Found: C, 51.27; H, 4.07.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)(OCHO) (12). A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(CH_3) (**11**, 0.47 g, 0.75 mmol),[35] benzene (20 mL), and a stir bar. Then 88% aqueous HCOOH (0.20 mL, 0.21 g, 4.7 mmol) was added with stirring. After 6 h, solvent was removed in vacuo and the flask was transferred to a glovebox. The red residue was extracted with benzene. The extract was filtered through a 2-cm silica gel plug with 50:50 (v/v) THF/hexane. Solvent was removed from the filtrate by rotary evaporation. The resulting oil was dissolved in toluene. Rotary evaporation gave crude **12** as a red powder. For an analytical sample, the oil was dissolved in 15 mL of CH_2Cl_2, layered with hexane, and kept at −40 °C for 2 days. Large orange crystals formed, which were collected by filtration and dried in vacuo to give **12**·$(CH_2Cl_2)_{0.5}$ (0.46 g, 0.66 mmol, 88%), mp 131–133 °C dec. Anal. Calcd for $C_{29.5}H_{32}ClNO_3PRe$: C, 50.53; H, 4.60. Found: C, 50.35; H, 4.65.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)(H) (13). A Schlenk flask was charged with **12** (0.22 g, 0.33 mmol), toluene (25 mL), and a stir bar and was fitted with a reflux condenser. The reaction was refluxed with stirring for 5 h, and solvent was then removed in vacuo. The flask was transferred to a glovebox, and the residue was extracted with benzene. The extract was filtered through a 2-cm silica gel plug, and solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was dissolved in ca. 10 mL of toluene, layered with hexane, and kept at −40 °C for 2 days. Red-orange crystals formed, which were collected by filtration and dried in vacuo to give **13** (0.097 g, 0.16 mmol, 48%), mp 189–190 °C. Anal. Calcd for $C_{28}H_{31}NOPRe$: C, 54.71; H, 5.08. Found: C, 54.73; H, 5.01.

Deprotonation of (η^5-C_5Me_5)Re(NO)(PPh_3)(H) (13). A Schlenk tube was charged with **13** (0.068 g, 0.12 mmol) and THF (0.75 mL) and the yellow solution was cooled to −78 °C. A second Schlenk tube was charged with K^+-*t*-BuO^- (0.022 g, 0.20 mmol), THF (0.50 mL), and a stir bar and was cooled to −78 °C. Then *n*-BuLi (0.14 mL, 1.4 M in hexane) was added to the second tube with stirring. After 15 min, **13** was added via a transfer needle. The solution immediately turned dark red. After 0.5 h, a THF solution (0.5 mL) of 18-crown-6 (0.048 g, 0.18 mmol) was added and the reaction was warmed to −24 °C. After 1.5 h, the reaction was cooled to −78 °C and CH_3I (0.037 g, 0.26 mmol) was added. After 10 min, the orange solution was warmed to room temperature, and solvents were removed in vacuo. The flask was transferred to a glovebox and the residue was extracted with benzene. The extract was filtered through a 3-cm silica gel plug, and solvent was removed from the filtrate by rotary evaporation. The resulting orange powder was dried in vacuo to give 0.066 g (0.10 mmol, 87%) of methylated products. A ^1H NMR spectrum showed the major product to be identical with an authentic sample of **11**.

Preparation of 2 from K^+-3/18-Crown-6. A Schlenk tube was charged with **1** (0.056 g, 0.10 mmol) and THF (1.0 mL) and cooled to −78 °C. A second Schlenk tube was charged with K^+-*t*-BuO^- (0.019 g, 0.17 mmol), THF (0.6 mL), and a stir bar and was cooled to −78 °C. Then *n*-BuLi (0.13 mL, 1.4 M in hexane) was added to the second tube with stirring. After 15 min, the yellow solution of **1** was added via a transfer needle. The solution immediately turned dark red. After 0.5 h, the reaction was warmed to −50 °C and a THF solution (0.5 mL) of 18-crown-6 (0.040 g, 0.015 mmol) was added via syringe to give K^+-**3**/18-crown-6. After 45 min, the reaction was cooled to −78 °C, and CH_3I (0.039 g, 0.27 mmol) was added to give a light orange solution. After 10 min, the solution was transferred to a round-bottom flask and solvents were removed by rotary evaporation. The residue was extracted with benzene and filtered. The benzene was removed by rotary evaporation. The resulting oil was dissolved in CH_2Cl_2 (1 mL), layered with hexane, and left at −24 °C for 3 days. Small orange crystals were collected and dried in vacuo to yield **2** (0.051 g, 0.092 mmol, 92%), mp 195–196 °C (lit.[13] mp 198–200 °C). A ^1H NMR spectrum was identical with that of an authentic sample of **2**.

Generation of $Li^+[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)]^-$ (Li^+-3) from 1 and $Li^{+}\,{}^{-}N(CH_3)_2$. A 5-mm NMR tube was charged with **1** (0.024 g, 0.044 mmol) and $Li^{+}\,{}^{-}N(CH_3)_2$ (0.0071 g, 0.14 mmol) and capped with a septum. A second 5-mm NMR tube was charged with THF-d_8 (0.30 mL) and capped with a septum. The tubes were immersed in a −15 °C bath and the THF-d_8 was added to the solid mixture via a transfer needle. The sample was periodically shaken over the course of 3 h to give a dark red, homogeneous solution. A ^{31}P NMR spectrum (−30 °C) showed the clean formation of Li^+-**3** (45.7 ppm, s).

Attempted Isolation of K^+/(18-Crown-6) $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)]^-$ (K^+-3/18-Crown-6). This procedure is representative of other attempts (detailed elsewhere)[25] to isolate M^+-**3**. Complex **1** (0.082 g, 0.15 mmol; in 3.0 mL of THF), K^+-*t*-BuO^- (0.030 g, 0.27 mmol; in 2.0 mL of THF), *n*-BuLi (0.19 mL, 1.4 M in hexane), and 18-crown-6 (0.067 g, 0.25 mmol; in 1.0 mL of THF) were combined as described in the preparation of **2** from K^+-**3**/18-crown-6. Then cold hexane (15 mL, −78 °C) was layered onto the dark red solution (−78 °C) via a transfer needle. The solution was kept at −78 °C, and over the course of 2 days a red precipitate formed. The solvents were removed via transfer needle and the red solid was transferred to a glovebox. The solid was collected and dried in vacuo. The sample was dissolved in THF at −78 °C, and a ^{31}P NMR spectrum (−28 °C) showed K^+-**3**/18-crown-6 (44.1 ppm, s, ca. 90%) and **1** (28.0 ppm, s, ca. 10%).

Monitoring of Reactions by ^{31}P NMR. The following experiments are representative. A 5-mm NMR tube was charged with **1** (0.018 g, 0.033 mmol) and THF (0.35 mL) and capped with a septum. A ^{31}P NMR spectrum was recorded at −61 °C (28.4 ppm, s). Then TMEDA (0.0040 g, 0.034 mmol) and *n*-BuLi (0.028 mL, 1.4 M in hexane) were added (−61 °C). The tube was shaken, and after 0.5 h a ^{31}P NMR spectrum was recorded at −61 °C (33.9 ppm, s, ca. 90%; 28.5 ppm, s, ca. 10%). The probe was warmed to −42 °C, and after 40 min a ^{31}P NMR spectrum was recorded (33.9 ppm, s, ca. 75%; 46.2 ppm, s, ca. 25%). The probe was warmed to −26 °C, and after 1 h a ^{31}P NMR spectrum was recorded (s, 44.5 ppm, 100%).

A 5-mm NMR tube was charged with **1** (0.016 g, 0.030 mmol) and THF (0.30 mL) and capped with a septum. A ^{31}P NMR spectrum was recorded at −24 °C (28.2 ppm, s). The tube was warmed to −15 °C, and TMEDA (0.0042 g, 0.036 mmol) and *n*-BuLi (0.025 mL, 1.4 M in hexane) were added. The tube was shaken and the contents changed from yellow to dark red. After 0.5 h, a ^{31}P NMR spectrum was recorded at −24 °C (45.1 ppm, s). The tube was immersed in a −24 °C bath, and $NH(Si(CH_3)_3)_2$ (0.014 g, 0.087 mmol) was added. The tube was shaken, and after 1 h a ^{31}P NMR spectrum was recorded at −24 °C (45.6 ppm, s, ca. 95%, Li^+-**3**; 28.1 ppm, s, ca. 5%, **1**). The tube was kept at −24 °C for 2 days. A ^{31}P NMR spectrum showed only **1** (27.8 ppm, s).

Preparation of Deuteriated Compounds. The key starting material (η^5-C_5D_5)Re(CO)$_3$ was prepared as previously reported.[33] Complex (η^5-C_5D_5)Re(NO)(PPh_3)(D) (**1**-d_6) was synthesized from $[(\eta^5$-$C_5D_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$, $(CH_3)_3N^+$–O^-, and $LiAlD_4$.[13] Complex (η^5-C_5D_5)Re(NO)(PPh_3)(H) (**1**-d_5) was prepared from **1**-d_6 analogously to the synthesis of **1**-d_1 from **1**.

Analysis of Labeling Experiments. The following experiment is representative, and others are detailed elsewhere.[25] A Schlenk tube was charged with **1** (0.024 g, 0.045 mmol), **1**-d_6 ((92 ± 2):(8 ± 2) d_6/d_5; 0.024 g, 0.043 mmol), THF (0.8 mL), and a stir bar and was cooled to −61 °C. Then TMEDA (0.013 g, 0.11 mmol) and *n*-BuLi (0.090 mL, 1.4 M in hexane) were added with stirring. After 1 h, the solution was warmed to −24 °C and stirred for an additional hour. Then CH_3I (0.046 g, 0.32 mmol) was added, and **2**-d_x was isolated as described for **2** above. The 70-eV mass spectrum of the product exhibited a *m/e* 557:558:559:560 ratio of 61.8:17.8:100.0:37.0 and a 562:563:564:565 ratio of 32.6:10.6:53.5:19.5. Under identical conditions, the *m/e* 557:558:559:560 ratio for natural abundance **2** was 55.5:16.6:100.0:24.1. These data indicate a **2**-d_0/**2**-d_1 ratio of (97 ± 2):(3 ± 2) and **2**-d_5/**2**-d_4 ratio of (94 ± 2):(6 ± 2).

Acknowledgment. We thank the Department of Energy for support of this research and the NSF for funds used to acquire the mass spectrometers employed.