

# Deprotonation and Anionic Rearrangements of Organometallic Compounds. Reactions of the Hydride Complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ with *n*-Butyl-lithium–Tetramethylethylenediamine

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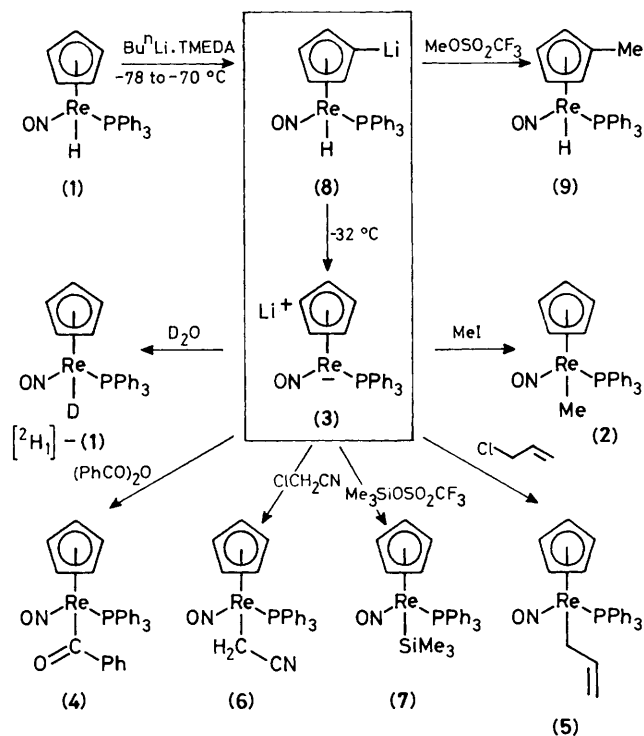
The title reaction ( $-71^\circ\text{C}$ ; 1 h) gives  $(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (**8**), which subsequently rearranges intramolecularly ( $-32^\circ\text{C}$ ; 0.5 h) to give  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  (**3**); the anions (**8**) and (**3**) are characterized by reactions with electrophiles.

Transition metal hydrides are ubiquitous in catalysis.<sup>1</sup> Yet, unlike carbon, nitrogen, and oxygen hydrides, the study of their acid–base properties is still in its infancy.<sup>2</sup> Fascinating base-dependent kinetic effects have been observed in the deprotonation of metal hydrides.<sup>2d</sup> We have begun to probe the acid–base chemistry of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$  complexes,<sup>3</sup> and report here our initial findings with the hydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (**1**). Remarkably, this compound exhibits completely divergent kinetic and thermodynamic acidity.

Reaction of (**1**)<sup>4</sup> with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  (1.1 equiv.; TMEDA = tetramethylethylenediamine) in tetrahydrofuran (THF) at  $-15^\circ\text{C}$  (10 min), followed by quenching with MeI, gave the methyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{Me})$  (**2**)<sup>4</sup> in 72% yield after work-up. The identity of the apparent precursor to (**2**), the anion  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  (**3**), was supported by additional trapping experiments with  $\text{D}_2\text{O}$ , benzoic anhydride, allyl chloride,  $\text{ClCH}_2\text{CN}$ , and  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ . The deuteride  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{D})$  [ $^2\text{H}_1$ ]-(**1**) (87%),<sup>5</sup> benzoyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{COPh})$  (**4**) (68%),<sup>6</sup> allyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CH}=\text{CH}_2)$  (**5**) (90%),<sup>†</sup> cyanomethyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CN})$  (**6**) (64%),<sup>†</sup> and silane complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{SiMe}_3)$  (**7**) (42%)<sup>†</sup> were subsequently isolated (Scheme 1).

Although (**3**) could plausibly be formed *via* simple Re–H deprotonation, our observations with analogous rhenium acyl complexes<sup>3</sup> prompted additional experiments. Treatment of 99.8% labelled [ $^2\text{H}_1$ ]-(**1**) with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  and MeI as above gave 99.7% labelled [ $^2\text{H}_1$ ]-(**2**), as determined by careful mass spectrometric analysis. This suggested that a proton was initially abstracted from the cyclopentadienyl ligand of (**1**) to give  $(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (**8**) (Scheme 1). Hence, the reaction of (**1**) with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  was monitored by  $^{31}\text{P}$  n.m.r. spectroscopy. During 1 h at  $-71^\circ\text{C}$ , (**1**) (28.2 p.p.m.) disappeared as a new resonance at 33.9 p.p.m. appeared. The mixture was then warmed to  $-32^\circ\text{C}$ , and during 0.5 h, the 33.9 p.p.m. resonance disappeared as a resonance at 47.2 p.p.m. appeared. In a separate experiment,  $\text{MeOSO}_2\text{CF}_3$  was added to the 33.9 p.p.m. intermediate ( $-42^\circ\text{C}$ ). A new product (29.1 p.p.m.; *ca.* 80%), and minor amounts of (**1**) and (**2**), were rapidly formed. This material was isolated in 52% yield by preparative silica gel h.p.l.c., and shown by spectral and microanalysis to be the methylation product of (**8**),  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (**9**).<sup>†</sup> We therefore conclude that (**8**) is the initial, 33.9 p.p.m., intermediate in the reaction of (**1**) with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$ . The 47.2 p.p.m. resonance is accordingly assigned to (**3**).

Attention was next turned to the molecularity and stereochemistry of the rearrangement (**8**) $\rightarrow$ (**3**). Co-reaction of a mixture of (**1**) and  $(\eta^5\text{-C}_5\text{D}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{D})$  [ $^2\text{H}_6$ ]-(**1**)



Scheme 1

(89%  $^2\text{H}_6$ , 11%  $^2\text{H}_5$ ) with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  ( $-61^\circ\text{C}$ , then  $-24^\circ\text{C}$ ) and MeI gave a 97:3 mixture of [ $^2\text{H}_0$ ]-(**2**) and [ $^2\text{H}_1$ ]-(**2**), and a 92:8 mixture of [ $^2\text{H}_3$ ]-(**2**) and [ $^2\text{H}_4$ ]-(**2**). Hence, proton migration is essentially intramolecular. Reaction of (+)-(*S*)-(**1**),<sup>5</sup> [ $\alpha$ ]<sub>589</sub><sup>25</sup> 33°, with  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  and MeI at  $-24^\circ\text{C}$  gave (+)-(*S*)-(**2**) (*retention*)<sup>7</sup> with [ $\alpha$ ]<sub>589</sub><sup>25</sup> 11°. Although the optical purity of the starting material is not certain, it is unlikely to be of  $< 40\%$  enantiomeric excess (e.e.).<sup>5</sup> The optical rotation of the product indicates a 6% e.e.<sup>7</sup> Thus the conversion (**1**) $\rightarrow$ (**2**) is accompanied by considerable racemization. Additional study is required to determine the step and/or intermediate responsible for this loss of stereospecificity.

Several aspects of the above observations are noteworthy. First, the stability order (**3**)  $>$  (**8**) indicates that the Re–H bond in (**1**) has a greater ion pair acidity than the cyclopentadienyl C–H bonds. Yet, the kinetic acidity is opposite. As a possible contributing factor, we note that (**3**) belongs to a class of metal anions which have recently been calculated to be ‘electronically destabilized.’<sup>2c</sup> Secondly, although the lithiation of  $\eta^5\text{-C}_5\text{H}_5$  ligands has been observed previously,<sup>3,9</sup> we are unaware of any reports of subsequent prototropic rearrangements. This constitutes a new, ‘ligand-assisted’ mechanism for metal hydride deprotonation. Other transformations

<sup>†</sup> Microanalytical, mass spectral, i.r., and n.m.r. ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) data for each new compound were provided for the referees.

analogous to (8) → (3) might be detected by use of suitably labelled precursors.<sup>10</sup> Thirdly, the C<sub>5</sub>H<sub>5</sub> ligand in (1) is deprotonated less readily than in analogous acyl complexes, and the hydride ligand subsequently migrates less readily than acyl ligands.<sup>3</sup> Further studies on the scope and mechanisms of these apparently quite general rearrangements are in progress. Finally, anions of the formula [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(L)]<sup>-</sup> have been inaccessible prior to this study.<sup>11</sup> These will be convenient precursors to new classes of organometallic complexes, as will be reported in the future.

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## References

- 1 G. W. Parshall, 'Homogeneous Catalysis,' Wiley, New York, 1980; C. Masters, 'Homogeneous Transition-metal Catalysis,' Chapman and Hall, New York, 1981.
- 2 (a) D. F. Shriver, *Acc. Chem. Res.*, 1970, **3**, 231; (b) R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc.*, 1982, **104**, 1255; (c) H. W. Walker, R. G. Pearson, and P. C. Ford, *ibid.*, 1983, **105**, 1179; (d) J. M. Hanckel and M. Y. Darensbourg, *ibid.*, 1983, **105**, 6979; (e) B. E. Bursten and M. G. Gatter, *ibid.*, 1984, **106**, 2554; *Organometallics*, 1984, **3**, 895, 941.
- 3 P. C. Heah and J. A. Gladysz, *J. Am. Chem. Soc.*, 1984, **106**, 7636.
- 4 W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, V. K. Wong, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 141.
- 5 J. H. Merrifield and J. A. Gladysz, *Organometallics*, 1983, **2**, 782.
- 6 W. E. Buhro, A. Wong, J. H. Merrifield, G.-Y. Lin, A. G. Constable, and J. A. Gladysz, *Organometallics*, 1983, **2**, 1852.
- 7 J. H. Merrifield, C. E. Strouse, and J. A. Gladysz, *Organometallics*, 1982, **1**, 1204.
- 8 This qualification is necessary since Li<sup>+</sup> is a component of the equilibrium (3) ⇌ (8): A. Streitwieser Jr., E. Juaristi, and L. L. Nebenzahl, in 'Comprehensive Carbanion Chemistry,' eds. E. Buncl and T. Durst, Elsevier, Amsterdam, 1980, p. 323. We presently have no quantitative data on the extent of ion pairing, so the formulae for (3) and (8) are approximations in Scheme 1.
- 9 See, *inter alia*: T. Yu. Orlova, V. N. Setkina, V. F. Sizoi, and D. N. Kursanov, *J. Organomet. Chem.*, 1983, **252**, 201; M. D. Rausch and D. J. Ciappenelli, *ibid.*, 1967, **10**, 127; N. E. Kolobova, Z. P. Valueva, and M. Ya. Solodova, *Bull. Acad. Sci. USSR*, 1980, 1701.
- 10 Depending upon the base and conditions, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ReH yields products formally derived from both carbon and rhenium deprotonation: R. L. Cooper, M. L. H. Green, and J. T. Moelwyn-Hughes, *J. Organomet. Chem.*, 1965, **3**, 261; R. I. Mink, J. J. Welter, P. R. Young, and G. D. Stucky, *J. Am. Chem. Soc.*, 1979, **101**, 6928. For reactions of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MH<sub>2</sub> (M = Mo, W) with Bu<sup>n</sup>Li, see B. R. Francis, M. L. H. Green, T. Luong-thi, and G. A. Moser, *J. Chem. Soc., Dalton Trans.*, 1976, 1339.
- 11 J. R. Sweet and W. A. G. Graham, *Organometallics*, 1982, **1**, 982.