Table V. Steepest Ascent Approach[a]

third series run no.	variable					response
	A_T, °C	A_t, h	T_c, equiv	T_T, °C	T_t, h	% yield
1	+17.5	1	1.3	−78	0	45.9
2	−17.5	2	1.3	−78	0	23.2
3	+17.5	2	1.3	−78	0	41.0
4	+35	$2^1/_2$	1.3	−78	0	37.0
5	+17.5	1	3.1	−35	1	63.3
6	+17.5	1	2.2	−78	0	52.6
7	0	$1^1/_2$	2.2	−78	0	3.5
8	−17.5	1	3.1	−78	0	77.7
9	−17.5	1	3.1	−78	0	72.1
10	+17.5	1	3.1	−78	0	77.1

[a] C was equal to 0.3 M in all cases.

Pentacarbonyl[2-oxacyclopentylidene]chromium (11). To a precooled (−78 °C) suspension of $K_2Cr(CO)_5$ (5 mmol) in THF (100 mL) under argon was added 4-chlorobutyryl chloride (0.705 g, 5 mmol) dropwise. The reaction was warmed to room temperature slowly overnight. After the mixture was filtered through Celite, the solvent was removed under reduced pressure, resulting in a dark brown solid. Purification by column chromatography (silica gel, 5% Et_2O–hexane) yielded the desired carbene as a yellow solid (0.710 g, 54%). This material was identical in all respects with that previously described.[12]

Pentacarbonyl[(dimethylamino)undecylcarbene]chromium (12). *N,N*-Dimethylundecylamide (910 mg, 4.0 mmol) was added to 48 mmol of $K_2Cr(CO)_5$ in 20 mL of THF at −78 °C, and the resulting mixture was stirred at that temperature for 1.25 h, warmed to 0 °C and stirred for 1 h, and cooled to −78 °C and stirred for 1.5 h. Trimethylsilyl chloride (12.0 mmol) was added, and the mixture was stirred at −78 °C for an additional $^1/_2$ h. After the mixture was warmed to room temperature, addition of Al_2O_3, removal of solvents, and column chromatography (silica gel; 1:1 hexane–CH_2Cl_2), 1.19 g (74%) of complex **12** was obtained as a pale green oil. ^{1}H NMR (270 MHz): δ 0.88 (t, J = 7.0 Hz, 3 H, CH_3), 1.19–1.24 (m, 18 H, CH_2), 3.03 (t, J = 7.8 Hz, 2 H, =CCH_2), 3.30 (s, 3 H, NCH_3), 3.82 (s, 3 H, NCH_3). ^{13}C NMR (67.9 MHz): δ 14.0 (CH_3), 22.7 (CH_3), 24.8 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 41.8 (=CCH_2), 52.8 (NCH_3), 53.3 (NCH_3), 218.0 (cis CO), 223.2 (trans CO), 277.8 (Cr=C). IR (film): ν 2855, 2051, 1907 cm^{-1}. MS (EI): m/z 403 (M^+), 375 (M^+ − CO), 347 (M^+ − 2CO), 291 (M^+ − 4CO), 263 (M^+ − 5CO).

Acknowledgment. Support for this research under Grant 2 RO1 GM26178-10 from the National Institutes of General Medical Sciences (Public Health Service) is gratefully acknowledged.

Registry No. 1, 38893-15-1; 2, 30971-68-7; 3, 117041-11-9; 4, 112044-06-1; 5, 129174-67-0; 6, 112044-04-9; 7, 129174-69-2; 8, 129174-69-2; 9, 112068-79-8; 10, 124685-64-9; 11, 54040-15-2; 12, 129174-70-5; C_8K, 12081-88-8; $Cr(CO)_6$, 13007-92-6; $K_2Cr(CO)_5$, 107799-34-8; dimethyl formamide, 68-12-2; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-dibenzylacetamide, 10479-30-8; (*S*)-2,2-dimethyl-4-phenyl-3-oxazolidinecarboxaldehyde, 112043-98-8; (*S*)-4-phenyl-3-oxazolidinecarboxaldehyde, 129174-66-9; morpholinoacetamide, 1696-20-4; *N,N*-diethyl-2-chlorobenzamide, 10345-79-6; *N,N*-diethyl-3-furancarboxamide, 73540-76-8; diphenylformamide, 607-00-1; 1-benzylpiperidin-2-one, 4783-65-7; 4-chlorobutyryl chloride, 4635-59-0; *N,N*-dimethyldodecylamide, 3007-53-2.

Reactions of the Cyanomethyl Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CN)$ and Ylide Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-tol})_3)]^+PF_6^-$ with *n*-BuLi/TMEDA: Generation, Stereospecific Alkylation, and Basicity of Transition-Metal-Substituted Carbanions and Ylides

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Reaction of the cyanomethyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CN)$ (**2**) with *n*-BuLi/TMEDA (THF, −78 °C) and then $CH_3OSO_2CF_3$ stereospecifically gives (*SR,RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CN)$ ((*SR,RS*)-**4**, 75%). Reaction of PPN^+CN^- and the ethylidene complex *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$ (*sc*-**8**) gives the opposite diastereomer, (*SS,RR*)-**4** (91%). The former reaction proceeds, as assayed by ^{31}P NMR spectroscopy and deuterium labeling, via the initial formation (ca. 2:1) of carbanions $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHCN)]^-$ (**5**) and $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_2CN)$ (**6**); **6** isomerizes to **5** thermally (−78 °C, 2.5 h) or upon addition of $CH_3OSO_2CF_3$. Complex **5** is the first observable transition-metal-substituted carbanion (IR (cm^{-1}): ν_{CN} 1980; ν_{NO} 1597) and is also stereospecifically alkylated by *n*-C_4H_9I. Equilibration reactions show the C_α acidity of **2** (THF) to be less than that of CH_3CN and comparable to that of CH_3CH_2CN. Reactions of (*SR,RS*)/(*SS,RR*)-**4** and *n*-BuLi/TMEDA give only cyclopentadienyl ligand lithiation. Reactions of the ylide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-tol})_3)]^+PF_6^-$ with *n*-BuLi/TMEDA (THF, −24 °C) and then $CH_3OSO_2CF_3$ (−78 °C) stereospecifically give (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)P(p\text{-tol})_3)]^+PF_6^-$ ((*SS,RR*)-**16**, 83%). This transformation proceeds, as assayed by ^{31}P NMR spectroscopy, via the ylide $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}P(p\text{-tol})_3)$. An authentic sample of (*SS,RR*)-**16** is prepared from *sc*-**8** and $P(p\text{-tol})_3$ (90%).

Organic reactive intermediates—e.g., carbanions, carbocations, radicals, carbenes—have been the focal point of innumerable studies over many years. There has been a roughly parallel development of the chemistry of transition-metal alkyl complexes. Surprisingly, little attention has been given to the generation of reactive intermediates

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on metal alkyl ligands.[1-5] It has been known for some time that carbanions and carbocations can be generated on a variety of π-complexed ligands.[1] Further, carbocations $L_nM-C^+R_2$ and $L_nM-CH_2-C^+HR$ are resonance contributors to cationic alkylidene and alkene complexes $[L_nM{=}CR_2]^+$ and $[L_nM(H_2C{=}CHR)]^+$.[2] However, few attempts have been made to generate carbanions,[3] radicals,[4] or carbenes[5] on alkyl ligands.

We wondered if it would be possible to deprotonate neutral, coordinatively saturated[6] metal alkyl complexes L_nMCH_2X at C_α, as shown in eq i. This would generate

$$L_nMCH_2X \xrightarrow[-(BH)]{B:^-} [L_nM\ddot{C}HX] \quad \text{(i)}$$

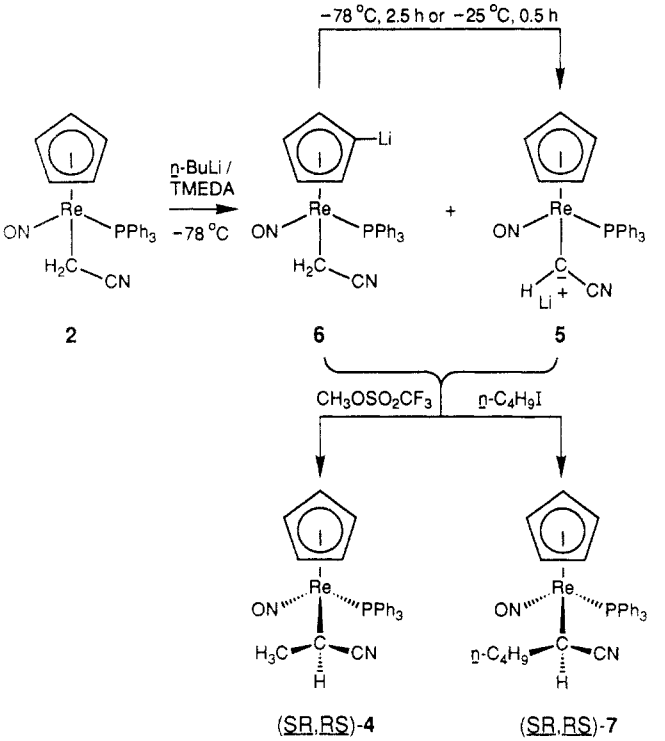
$$L_nMCH_2\overset{+}{P}Ar_3 \xrightarrow[-(BH)]{B:^-} L_nM\ddot{C}H-\overset{+}{P}Ar_3 \longleftrightarrow L_nMCH{=}PAr_3 \quad \text{(ii)}$$

transition-metal-substituted carbanions, the properties of which would be of considerable fundamental interest. Such reactions, and the target complexes, were without precedent at the outset of this study. However, Schrock had reported the deprotonation of the *cationic*, coordinatively *un*saturated tantalum methyl complex $[(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2]^+$ to the methylidene complex $(\eta^5\text{-}C_5H_5)Ta(=CH_2)(CH_3)$.[7]

As a tandem objective, we sought to study the deprotonation chemistry of a related *cationic* class of compounds, "phosphorus ylide" complexes $[L_nMCH_2PAr_3]^+$.[8] As shown in eq ii, C_α deprotonation would yield a transition-metal-substituted ylide or Wittig reagent.[9] While several examples of such compounds have been reported,[8,10] none have to our knowledge been prepared from a detectable ylide complex precursor.

We have previously shown that the chiral rhenium methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and *n*-BuLi/TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) react to give the lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_3)$.[11] Hence, we sought to study reactions of strong bases and (1) alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2X)$ that bear carbanion-stabilizing C_α substituents and (2) analogous cationic phosphorus ylide complexes. We further sought to assay whether any C_α deprotonation products would show, as a consequence of the chiral metal substituent, significant diastereoselection in subsequent reactions. In this paper, we describe the generation, stereospecific alkylation, and physical properties of rhenium-substituted carbanions and ylides. Portions of this study have been communicated.[12]

Scheme I. Generation and Stereospecific Alkylation of the Rhenium-Substituted Carbanion $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{C}HCN)]^-$ (5)



Results

1. Synthesis of a Rhenium Cyanomethyl Complex. Cyano groups are powerful carbanion-stabilizing substituents. Thus, cyano-substituted alkyl complexes were sought for initial study. The nucleophilic "rhenium anion" $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**1**) has been shown to be a convenient precursor to a variety of alkyl complexes.[13] Hence, **1** and the alkylating agent $ClCH_2CN$ were combined at −78 °C. Workup gave the cyanomethyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CN)$ (**2**, eq iii) in 68% yield.

An alternative route to **2**, relevant to other syntheses described below, was also investigated. The methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**) has been found to readily undergo C_α attack by a variety of nucleophiles.[14] Accordingly, reaction of **3** and the cyanide salt PPN^+CN^- (eq iii)[15] gave **2** in 88% yield.[16a]

(1) (a) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, section 59.13. (b) Pearson, A. J.; Khetani, V. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1772.

(2) (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (c) Approaches to C_γ carbocations $L_nM-CH_2-CH_2-CHR^+$: Casey, C. P.; Smith, L. J. *Organometallics* **1988**, *7*, 2419. Brookhart, M.; Liu, Y. *Ibid.* **1989**, *8*, 1569.

(3) (a) van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 5191; **1987**, *28*, 6493. (b) Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640. (c) Wanat, R. A.; Collum, D. B. *Organometallics* **1986**, *5*, 120. (d) Kneuper, H.-J.; Zimmermann, C.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 1043.

(4) Good evidence exists for radicals of the type $L_nMCH_2\dot{C}HR$ as intermediates in certain alkene addition reactions; see for example: Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

(5) (a) Gallop, M. A.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1002. (b) Murahashi, S. I.; Kitani, Y.; Uno, T.; Hosokawa, T.; Miki, K.; Yonezawa, T.; Kasai, N. *Organometallics* **1986**, *5*, 356. (c) Menu, M. J.; Desrosiers, P.; Dartiguenave, M.; Dartiguenave, Y.; Bertrand, G. *Ibid.* **1987**, *6*, 1822.

(6) The C_α deprotonation of *neutral* coordinately *un*saturated metal alkyl complexes would most likely, due to the presence of metal-based acceptor orbitals, give anionic carbene complexes $[L_nM{=}CHX]^-$.

(7) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(8) (a) Weber, L. In *The Chemistry of the Metal-Carbon Bond*; Hartley, H. R. Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, Chapter 3. (b) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (c) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(9) Discussion of eq ii is potentially confusing, as a "phosphorus ylide complex" reactant is deprotonated to a phosphorus ylide product! We have chosen not to modify these nomenclature conventions, since both are well entrenched in the literature.

(10) (a) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289. (b) Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207. (c) Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310. (d) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Ibid.* **1985**, *4*, 2059. (e) Arzoumanian, H.; Baldy, A.; Lai, R.; Metzger, J.; Peh, M.-L. N.; Pierrot, M. *J. Chem. Soc. Chem. Commun.* **1985**, 1151. (f) Cramer, R. E.; Bruck, M. A.; Edelmann, F.; Afzal, D.; Gilje, J. W.; Schmidbaur, H. *Chem. Ber.* **1988**, *121*, 417.

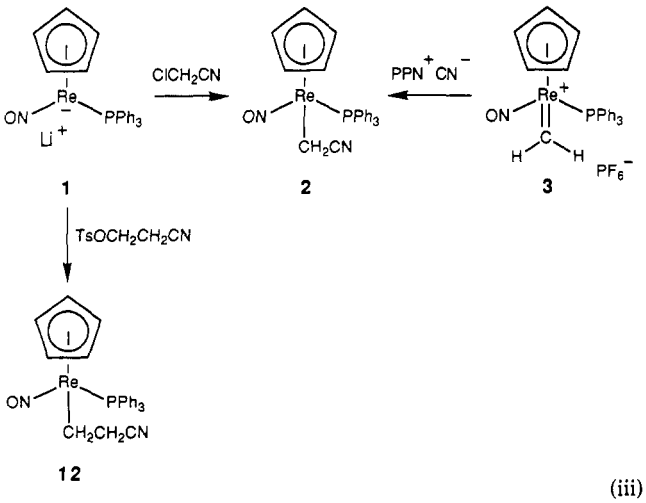
(11) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *106*, 1185.

(12) (a) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103. (b) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154.

(13) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

(14) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(15) Abbreviations: $PPN^+ = [Ph_3P{=}N{=}PPh_3]^+$; $-OTs = -OSO_2\text{-}p\text{-}C_6H_4CH_3$.



(iii)

Complex **2**, and all other new compounds isolated below, were characterized by microanalysis (Experimental Section), and IR, NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), and mass spectroscopy (Table I). The IR spectrum of **2** showed ν_{NO} at 1648 cm^{-1} (s) and ν_{CN} at 2197 cm^{-1} (m). The cyclopentadienyl ligand ^{1}H and ^{13}C NMR chemical shifts, and PPh_3 ligand ^{31}P NMR chemical shift, were characteristic of neutral (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes. The cyanide ^{13}C NMR resonance (133 ppm) was slightly downfield of those found in organic nitriles (112–126 ppm).[16b]

2. Synthesis and Reactivity of a Rhenium-Substituted Carbanion. The cyanomethyl complex **2** was treated with the strong base *n*-BuLi/TMEDA (1.0 equiv) in THF at −78 °C. Subsequent addition of the methylating agent $CH_3OSO_2CF_3$ gave the α-cyanoethyl complex (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CN) ((*SR,RS*)-**4**)[17] in 75% yield after workup (Scheme I). The gross structure of (*SR,RS*)-**4** followed readily from spectroscopic properties (Table I), and the stereochemistry was assigned as described below. Both NMR and HPLC analysis of the crude reaction mixture and purified product showed <1% of the opposite diastereomer, (*SS,RR*)-**4**, to be present.

Evidence was sought for the apparent precursor to (*SR,RS*)-**4**, the rhenium-substituted carbanion Li$^+$[(η^5-C_5H_5)Re(NO)(PPh_3)(C̈HCN)]$^-$ (**5**). Thus, the reaction of **2** and *n*-BuLi/TMEDA was monitored by ^{31}P NMR spectroscopy at −98 °C. The starting material (22.0 ppm) immediately disappeared, and two products appeared in a (62 ± 5):(38 ± 5) ratio (32.1 ppm, br; 25.7 ppm, sh).[18] No major spectral change was observed over the course of 3 h. When the sample was warmed (−78 °C, 2.5 h or −25 °C, 0.5 h), the 25.7 ppm resonance disappeared and the 32.1 ppm resonance sharpened. When the warmed samples were again cooled (−98 °C, 3 h), the spectrum was unaffected. Addition of $CH_3OSO_2CF_3$ to any of these solutions (−98, −78, −25 °C) gave exclusively (*SR,RS*)-**4**, as assayed by ^{31}P NMR spectroscopy.

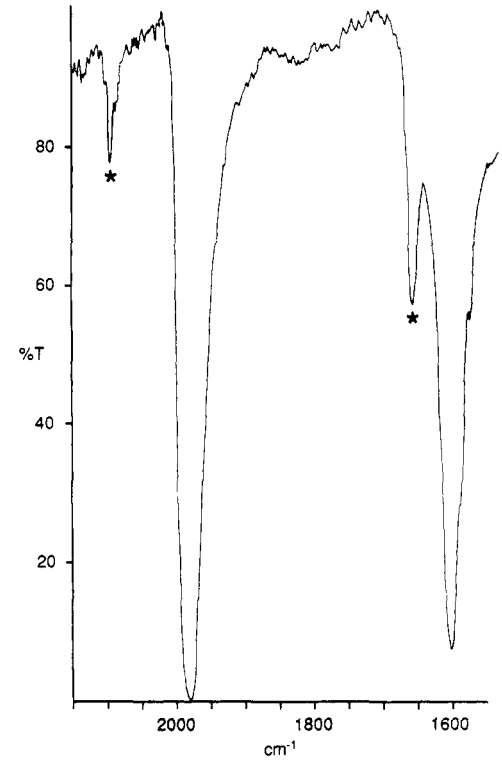


Figure 1. IR spectrum of the rhenium-substituted carbanion Li$^+$[(η^5-C_5H_5)Re(NO)(PPh_3)(C̈HCN)]$^-$ (**5**). Impurity peaks due to the corresponding alkyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CN) (**2**) are designated by asterisks.

Deuterium labeling studies were conducted to provide additional informtion on the intermediates observed by ^{31}P NMR spectroscopy. The dideuteriocyanomethyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CD_2CN) (**2**-d_2; (91 ± 2):(9 ± 2) d_2/d_1) was treated with *n*-BuLi/TMEDA and $CH_3OSO_2CF_3$ as in Scheme I. Workup gave a (31 ± 2):(69 ± 2) (*SR,RS*)-**4**-d_2/(*SR,RS*)-**4**-d_1 mixture, as assayed by mass spectrometry. No d_2 product would be expected if the cyanomethyl ligand were the exclusive site of deprotonation. Hence, an identical reaction was conducted with the pentadeuteriocyclopentadienyl complex (η^5-C_5D_5)Re(NO)(PPh_3)(CH_2CN) (**2**-d_5; (86 ± 2):(14 ± 2) d_5/d_4). Workup gave a (62 ± 2):(38 ± 2) (*SR,RS*)-**4**-d_5/(*SR,RS*)-**4**-d_4 mixture. These data show that *n*-BuLi/TMEDA deprotonates both the cyanomethyl and cyclopentadienyl ligands of **2**, with the former dominating. Accordingly, the 32.1 ppm ^{31}P NMR resonance noted above is assigned to the C_α carbanion Li$^+$[(η^5-C_5H_5)Re(NO)(PPh_3)(C̈HCN)]$^-$ (**5**), and the 25.7 ppm resonance is assigned to the lithiocyclopentadienyl complex (η^5-C_5H_4Li)Re(NO)(PPh_3)(CH_2CN) (**6**).

The lithiation of cyclopentadienyl ligands in (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes has abundant precedent.[11,12,19] As observed with **2** → **6**, a 2–5 ppm downfield ^{31}P NMR shift commonly occurs. However, all attempts to trap **6** were unsuccessful. In a ^{31}P NMR monitored experiment, 0.5 equiv of $CH_3OSO_2CF_3$ was added to a mixture of **5** and **6** at −78 °C (where equilibration is normally slow). A mixture of **5** and the α-cyanoethyl complex (*SR,RS*)-**4** rapidly formed. No other resonances were observed. Hence, (*SR,RS*)-**4** (and/or an impurity in the $CH_3OSO_2CF_3$) promotes the equilibration of carbanions **5** and **6**. Such equilibrations are common in reactions of

(16) (a) A similar reaction has been independently reported: McCormick, F. B. *Organometallics* **1984**, *3*, 1924. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; pp 159–161.

(17) Absolute configurations are assigned according to the Baird–Sloan modification of the Cahn–Ingold–Prelog priority rules. The η^5-C_5H_5 ligand is considered to be a pseudoatom of atomic number 30, which gives the following sequence: η^5-C_5H_5, η^5-C_5H_4R > PPh_3 > NO > CHRX. The rhenium configuration is specified first. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Sterechem.* **1981**, *12*, 1.

(18) 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 ^{1}H NMR integrations and quantitative ^{31}P NMR experiments.[13] The following ^{31}P T_1 values were measured (s): **2**, 0.429; **5**, 0.525; **6**, 0.287.

(19) (a) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 910. (b) Crocco, G. L.; Gladysz, J. A. *Chem. Ber.* **1988**, *121*, 375. (c) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158.

Table I. Spectroscopic Characterization of New Rhenium Complexes

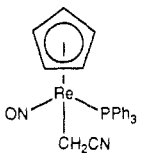
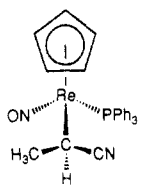
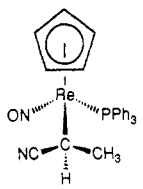
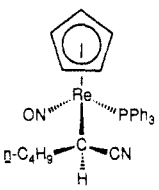
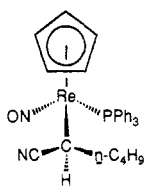
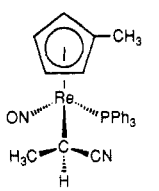
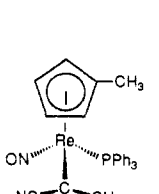
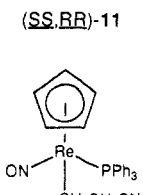
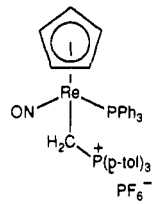
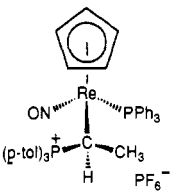
complex	IR (KBr), cm^{-1}	^1H NMR, δ[a]	$^{13}C\{^1H\}$ NMR, ppm[b]	$^{31}P\{^1H\}$ NMR, ppm[c]	mass spectrum (^{187}Re), m/z[d]
 **2**	ν_{NO} 1648 s; ν_{CN} 2197 m	7.47–7.31 (m, 3 C_6H_5); 5.12 (s, C_5H_5); 2.55 (dd, J = 15.5, 5.7 (HP), C*H*H′); 1.93 (dd, J = 15.5, 3.8 (HP), CH*H*′)	133.0 (s, CN); PC_6H_5 at 135.8 (d, J = 52.4, *i*), 131.2 (s, *p*), 131.1 (d, J = 10.2), 129.3 (d, J = 10.9); 91.5 (s, C_5H_5); −41.4 (d, J = 4.2, ReC)	21.1 (s)	584 (M^+, 55%); 554 (M^+ − CH_2CN, 100%); 437 (M^+ − CH_2CN − NO − C_6H_5, 5%); 435 (M^+ − NO − CH_2CN − C_6H_5 − H_2, 15%); 262 (PPh_3^+, 21%)
 (SR,RS)-**4**	ν_{NO} 1639 s; ν_{CN} 2194 m	7.45–7.39 (m, 3 C_6H_5); 5.11 (s, C_5H_5); 2.86 (dq, J = 7.0, 7.0 (HP), ReCH); 1.70 (d, J = 6.9, CH_3)	134.1 (s, CN); PC_6H_5 at 136.1 (d, J = 53.3, *i*), 134.5 (d, J = 10.6), 131.3 (d, J = 2.2, *p*), 129.4 (d, J = 10.7); 92.3 (s, C_5H_5); 29.0 (d, J = 2.3, CH_3); −23.9 (d, J = 3.8, ReC)	21.9 (s)	598 (M^+, 45%); 544 (M^+ − $CHCH_3CN$, 100%); 437 (M^+ − $CHCH_3CN$ − NO − C_6H_5, 5%); 435 $CHCH_3CN$ − NO − C_6H_5 − H_2, 15%); 262 (PPh_3^+, 12%)
 (SS,RR)-**4**	ν_{NO} 1632 s; ν_{CN} 2187 m	7.45–7.29 (m, 3 C_6H_5); 5.13 (s, C_5H_5); 2.80 (dq, J = 7.3, 4.2 (HP), ReCH); 1.23 (d, J = 7.4, CH_3)	135.9 (d, J = 4.3, CN); PC_6H_5 at 136.1 (d, J = 53.2, *i*), 134.2 (d, J = 9.5), 131.3 (s, *p*), 129.4 (d, J = 9.5); 92.3 (s, C_5H_5); 25.6 (s, CH_3); −25.7 (s, ReC)	21.2 (s)	598 (M^+, 32%); 544 (M^+ − $CHCH_3CN$, 100%); 514 (M^+ − $CHCH_3CN$ − NO, 4%); 437 (M^+ − $CHCH_3CN$ − NO − C_6H_5, 6%); 435 $CHCH_3CN$ − NO − C_6H_5 − H_2, 17%); 336 (M^+ − PPh_3, 6%); 262 (PPh_3^+, 81%)
 (SR,RS)-**7**	ν_{NO} 1647 s; ν_{CN} 2191 m	7.46–7.38 (m, 3 C_6H_5); 5.10 (s, C_5H_5); 2.78 (dt, J = 6.0, 9.5, ReCH);[e] 1.77 (m, CH_2); 1.27 (m, 2 CH_2); 0.86 (t, J = 7.1, CH_3)	133.2 (s, CN); PC_6H_5 at 135.9 (d, J = 53.2, *i*), 134.4 (d, J = 9.6), 131.1 (s, *p*), 129.3 (d, J = 10.8); 92.2 (s, C_5H_5); *n*-C_4H_9 (s) at 43.2, 34.8, 22.4, 14.2; −16.2 (d, J = 2.5, ReC)	21.4 (s)	640 (M^+, 33%); 597 (M^+ − C_3H_7, 7%); 544 (M^+ − $CH(C_4H_9)CN$, 100%); 437 (M^+ − $CH(C_4H_9)CN$ − NO − C_6H_5, 6%); 435 (M^+ − $CH(C_4H_9)CN$ − NO − C_6H_5 − H_2, 18%); 378 (M^+ − PPh_3, 35%); 262 (PPh_3^+, 19%)
 (SS,RR)-**7**	ν_{NO} 1659 s; ν_{CN} 2190 m	7.45–7.28 (m, 3 C_6H_5); 5.13 (s, C_5H_5); 2.68 (ddd, J = 12, 4, 4 (HP), ReCH);[e] 1.28 (m, CH_2); 1.01 (m, CH_2); 0.78 (m, CH_2); 0.68 (t, J = 7.0 Hz, CH_3)	134.7 (s, CN); PC_6H_5 at 136.0 (d, J = 51.4, *i*), 134.3 (d, J = 9.5), 131.2 (s, *p*), 129.4 (d, J = 11.3); 92.1 (s, C_5H_5); *n*-C_4H_9 (s) at 40.3, 35.5, 22.0, 14.1; −17.8 (s, ReC)	21.2 (s)	640 (M^+, 23%); 597 (M^+ − C_3H_7, 5%); 544 (M^+ − $CH(C_4H_9)CN$, 100%); 437 (M^+ − $CH(C_4H_9)CN$ − NO − C_6H_5, 8%); 435 (M^+ − $CH(C_4H_9)CN$ − NO − C_6H_5 − H_2, 20%); 378 (M^+ − PPh_3, 25%); 262 (PPh_3^+, 93%)
 (SR,RS)-**11**	ν_{NO} 1650 s; ν_{CN} 2187 m	7.46–7.37 (m, 3 C_6H_5); C_5H_4 (br m) at 5.47, 5.29, 4.46, 4.27; 2.90 (dq, J = 6.6, 6.6 (HP), ReCH); 2.19 (s, $C_5H_4CH_3$); 1.72 (d, J = 6.9, $CH(CH_3)CN$)	134.3 (s, CN); PC_6H_5 at 136.2 (d, J = 53.1, *i*), 134.5 (d, J = 10.8), 131.2 (d, J = 2.1, *p*), 129.4 (d, J = 10.3); C_5H_4 at 106.2 (d, J = 3.6, *i*), 96.3 (s), 94.4 (d, J = 3.8), 92.2 (s), 88.0 (s); 28.9 (d, J = 2.4, $CH(CH_3)CN$); 14.0 (s, $C_5H_4CH_3$); −23.1 (d, J = 3.5, ReC)	23.4 (s)	612 (M^+, 39%); 558 (M^+ − $CHCH_3CN$, 100%); 449 (M^+ − $CHCH_3CN$ − NO − $C_5H_4CH_3$, 9%); 350 (M^+ − PPh_3, 3%); 262 (PPh_3^+, 35%)
 (SS,RR)-**11**	ν_{NO} 1649 s; ν_{CN} 2187 m	7.45–7.29 (m, 3 C_6H_5); C_5H_4 (br m) at 5.40, 5.28, 4.57, 4.28; 2.78 (dq, J = 7.3, 4.4 (HP), ReCH); 2.21 (s, $C_5H_4CH_3$); 1.21 (d, J = 7.4, $CH(CH_3)CN$)	135.0 (s, CN); PC_6H_5 at 135.5 (d, J = 51.2, *i*), 133.6 (d, J = 6.9), 130.5 (s, *p*), 128.7 (d, J = 9.3); C_5H_4 at 107.1 (d, J = 3.8, *i*), 94.9 (d, J = 3.6), 94.4 (s), 90.2 (s), 86.9 (s); 25.0 (d, J = 5.5, $CH(CH_3)CN$); 13.4 (s, $C_5H_4CH_3$); −24.8 (d, J = 3.8, ReC)	22.3 (s)	612 (M^+, 23%); 558 (M^+ − $CHCH_3CN$, 90%); 449 (M^+ − $CHCH_3CN$ − NO − $C_5H_4CH_3$, 8%); 262 (PPh_3^+, 58%)
 **12**	ν_{NO} 1627 s; ν_{CN} 2233 m	7.30–7.50 (m, 3 C_6H_5); 4.99 (s, C_5H_5); CH_2CH_2 (m, 1 H) at 2.76, 2.60, 2.35, 1.90[g]	124.2 (s, CN); PC_6H_5 at 135.6 (d, J = 53.1, *i*), 133.3 (s, J = 11.4), 130.1 (s, *p*), 128.3 (d, J = 10.5); 89.5 (s, C_5H_5); 27.6 (d, J = 3.6, CH_2CN); −17.2 (d, J = 6.2, $ReCH_2$)[g]	24.5 (s)[g]	599 (M^+, 100%); 559 (M^+ − CH_2CN, 33%); 545 (M^+ − CH_2CH_2CN, 48%); 307 (M^+ − PPh_3 − NO, 24%); 279 (M^+ − PPh_3 − NO − CH_2CH_2, 43%); 262 (PPh_3^+, 31%)[h]

Table I (Continued)

complex	IR (KBr), cm^{-1}	^1H NMR, δ[a]	$^{13}C\{^1H\}$ NMR, ppm[b]	$^{31}P\{^1H\}$ NMR, ppm[c]	mass spectrum (^{187}Re), m/z[d]
 **14**	ν_{NO} 1665 s	7.49–7.29 (m, 3 C_6H_5, 3 C_6H_4R); 4.70 (s, C_5H_5); 3.04 (ddd, J = 14.4, 9.3 (HP), 9.3 (HP), ReCH*H*′); 2.83 (dd, J = 15.0, 15.0 (HP), ReCH*H*′); 2.41 (s, 3 CH_3)[g]	C_{aryl} at 144.0 (s, PC_6H_4R *p*), 130.8 (s, PC_6H_5 *p*), 134.4 (PC_6H_5 *i*),[f] 121.1 (d, J = 85.7, PC_6H_4R *i*), 133.8 (d, J = 10.0), 133.5 (d, J = 8.6), 130.0 (d, J = 11.7), 128.8 (d, J = 10.2); 90.5 (s, C_5H_5); 21.6 (s, $PC_6H_4CH_3$); −29.6 (d, J = 34.3, ReC)[g]	40.2 (d, J = 17.9, PC_6H_4R); 20.8 (d, J = 17.8, PC_6H_5)[g]	862 (M^+, 40%); 558 (M^+ − $P(C_6H_4CH_3)_3$, 100%); 467 (M^+ − $CH_2P(C_6H_4CH_3)_3$ − C_6H_5, 12%); 435 (M^+ − $CH_2P(C_6H_4CH_3)_3$ − C_6H_5 − H_2, 4%)[h]
 (SS,RR)-**16**	ν_{NO} 1667 s	7.53–7.26 (m, 3 C_6H_5, 3 C_6H_4R); 4.79 (s, C_5H_5); 3.64 (apparent sept, J = 7.0, ReCH); 2.41 (s, 3 $C_6H_4CH_3$); 1.46 (dd, J = 7.7, 21.4 (HP), ReCHCH_3)[g]	C_{aryl} at 143.9 (d, J = 3.0, PC_6H_4R *p*), 130.7 (d, J = 2.7, PC_6H_5 *p*), 132.7 (PC_6H_5 *i*),[f] 119.7 (d, J = 81.9, PC_6H_4R *i*), 133.3 (d, J = 12.9), 133.2 (d, J = 10.1), 130.2 (d, J = 11.4), 128.7 (d, J = 9.4); 90.6 (s, C_5H_5); 23.5 (d, J = 1.7, ReCHCH$_3$); 21.6 (d, J = 2.3, $PC_6H_4CH_3$); −12.8 (dd, J = 26.1, 1.9, ReC)[g]	43.0 (d, J = 17.0, PC_6H_4R); 19.7 (d, J = 16.9, PC_6H_5)[g]	876 (M^+, 2%); 861 (M^+ − CH_3, 4%); 572 (M^+ − $P(C_6H_4CH_3)_3$, 100%); 544 (M^+ − $CHCH_3P$ − $(C_6H_4CH_3)_3$, 35%); 467 (M^+ − $CHCH_3P(C_6H_4CH_3)_3$ − C_6H_5, 10%); 435 (M^+ − $CHCH_3P(C_6H_4CH_3)_3$ − NO − C_6H_5 − H_2, 8%)[h]

[a] Recorded in CD_2Cl_2 at 300 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$ unless noted; all couplings (Hz) are to hydrogen unless noted. [b] Recorded in CD_2Cl_2 at 75 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$ unless noted; all couplings (Hz) are to phosphorus. [c] Recorded in CD_2Cl_2 at 32.2 MHz and ambient probe temperature and referenced to external 85% H_3PO_4 unless noted; all couplings (Hz) are to phosphorus. [d] Electron impact (70 eV) unless noted. [e] The ReCH ^1H NMR resonance of (*SS,RR*)-**4** is an apparent dt; J values were assigned from ^1H and ^{31}P decoupling experiments. Similar experiments were not conducted for the ReCH resonance of (*SR,RS*)-**4** (also an apparent dt), but probable assignments are J_{HH} = 9.5, 5.9 Hz, J_{HP} = 5.9 Hz. [f] One line of doublet; other line obscured by other phenyl resonances. [g] Spectrum recorded in $CDCl_3$. [h] (+)-FAB (Ar, 7 kV, 3-nitrobenzyl alcohol).

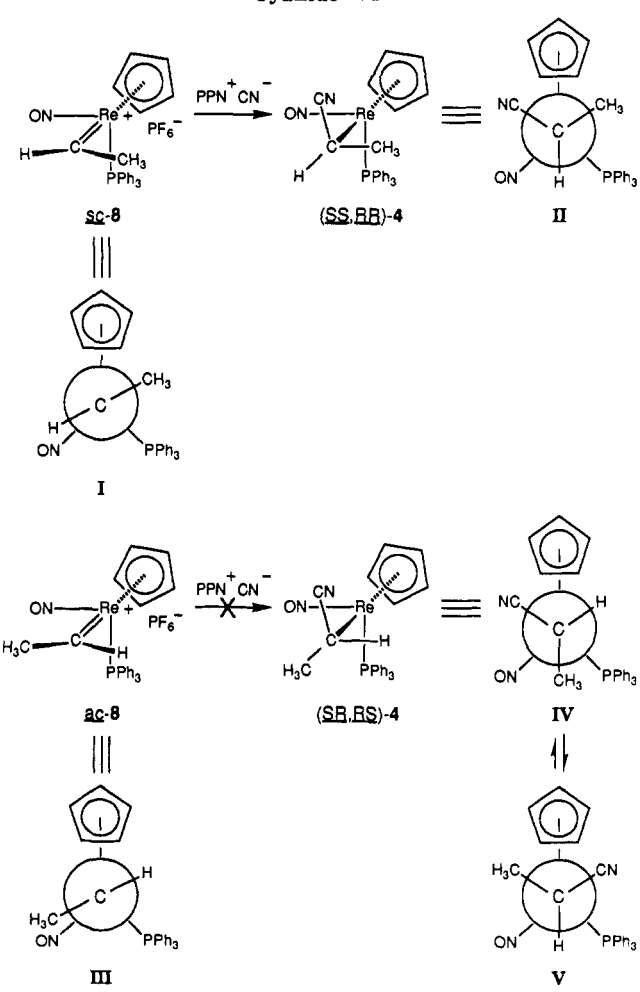
enolate anions with alkylating agents.[20a]

The C_α carbanion **5** decomposed over the course of 0.5 h at −15 °C to the cyanomethyl complex **2** and insoluble material. A low-temperature IR spectrum of **5** (−18 °C, THF)[21] showed ν_{CN} (1980 cm^{-1} s) and ν_{NO} (1597 cm^{-1} s) at considerably lower frequencies than in **2** (Figure 1).

Reaction of **2** with *n*-BuLi/TMEDA (THF, −78 °C) and then *n*-C_4H_9I gave the α-cyanopentyl complex (*SR,RS*)-$(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)(CH(*n*-C_4H_9)CN) ((*SR,RS*)-**7**) in 53% yield after workup (Scheme I). Product stereochemistry was established as described below, and NMR and HPLC analysis of the crude product showed <1% of the opposite diastereomer, (*SS,RR*)-**7**, to be present. The C_α carbanion **5** was slowly added ("inverse" addition)[20b] to excess CF_3COOD at −24 °C. Workup gave the deuteriocyanomethyl complex $(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)(CHDCN) (**2**-d_1) as a (68 ± 2):(32 ± 2) mixture of diastereomers, as assayed by ^1H NMR spectroscopy. Deuterium was preferentially incorporated into the upfield H_α proton.

3. Stereochemistry of Carbanion Alkylation. Nucleophiles preferentially attack C_α of alkylidene complexes $[(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)(=CHR)]$^+X^-$ from a direction anti to the PPh_3 ligand.[22] Hence, we sought to prepare authentic samples of the diastereomers of **4** by cyanide ion attack upon the two Re=C isomers of the ethylidene complex $[(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (**8**).[22b] As illustrated in Scheme II, reaction of the less stable Re=C isomer, *sc*-**8**, with PPN^+CN^- gave the α-cyanoethyl

Scheme II. Reactions of the Ethylidene Complex $[(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (8) with Cyanide Ion

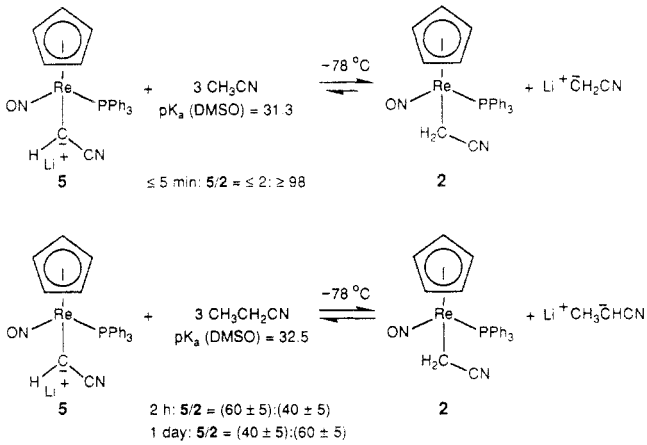


(20) (a) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: Menlo Park, CA, 1972; pp 564–570. (b) *Ibid.*, pp 498–508.

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

(22) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *Ibid.* **1983**, *105*, 4958. (c) Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879. (d) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837.

Scheme III. Reactions of the Rhenium-Substituted Carbanion 5 with Weak Acids: Estimation of the Acidity of Cyanomethyl Complex 2 in THF



complex (*SS,RR*)-**4** in 91% yield after workup. This compound differed from the methylation product obtained in Scheme I, as shown by the spectral data in Table I. Thus, the product in Scheme I must be (*SR,RS*)-**4**.

Interestingly, the more stable ethylidene complex Re=C isomer, *ac*-**8**, did not react with PPN^+CN^- in refluxing CH_2Cl_2 (Scheme II). This compound is commonly utilized as a (90 ± 2):(10 ± 2) *ac*-**8**/*sc*-**8** equilibrium mixture, and $\Delta G^{\ddagger}_{298}$ for *ac*-**8** → *sc*-**8** is 21.0 kcal/mol.[22b] When this reaction was monitored by ^{31}P NMR spectroscopy at −78 or 20 °C, only the minor, less stable Re=C isomer *sc*-**8** was consumed to give (*SS,RR*)-**4**.

As a check on the thermodynamics of the attempted PPN^+CN^- addition to *ac*-**8**, the α-cyanoethyl complex (*SR,RS*)-**4** was treated with $PPN^+PF_6^-$. No reaction occurred after 2 days in CH_2Cl_2 at 40 °C or 3 days in toluene at 110 °C. The diastereomers (*SR,RS*)- and (*SS,RR*)-**4** showed no decomposition or equilibration over the course of 4 days in toluene at 110 °C and only slight decomposition after 1 day in CD_3CN at 82 °C.

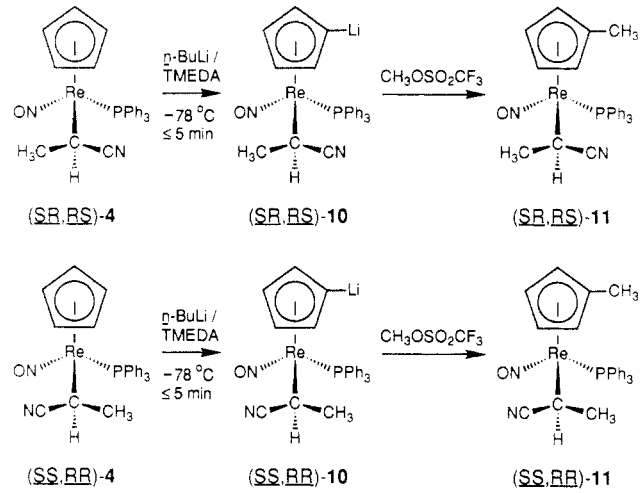
Finally, the stereochemistry assigned to the α-cyanopentyl complex (*SR,RS*)-**7** in Scheme I was also checked. Reaction of the less stable pentylidene complex Re=C isomer *sc*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_2CH_2CH_3$)]$^+PF_6^-$ (*sc*-**9**)[22b] and PPN^+CN^- gave the opposite diastereomer, (*SS,RR*)-**7**, in 72% yield after workup.

4. Estimation of Acidities. We sought to determine the effect of the (η^5-C_5H_5)Re(NO)(PPh_3) substituent on the acidity of the C_α protons in the cyanomethyl complex **2**. Thus, in a ^{31}P NMR monitored experiment, a THF solution of C_α carbanion **5** was treated with 3.0 equiv of carefully purified CH_3CN at −78 °C. Immediate conversion to **2** occurred (Scheme III). As little as 2% of unreacted **5** would have been detected. This experiment was repeated with CD_3CN. The product was isolated and shown to be deuterated at C_α. This established that **5** was not quenched by adventitious proton sources.

The **5**/CD_3CN reaction mixture was kept at 25 °C for 8 h. The resulting cyanomethyl complex **2**-d_x was extensively deuterated (d_0:d_1:d_2:d_3:d_4:d_5:d_6:d_7 = <1:6:12:20:31:21:9:1), as assayed by mass spectrometry. The peak patterns in the $M^+ - CH_xD_yCN$ and PPh_3^+ ions (Table I) indicated that the surplus deuterium had been incorporated into the cycopentadienyl ligand. Hence, additional exchange between the cyclopentadienyl protons of **2**-d_x and the base generated, $Li^+CD_2CN^-$, must have occurred. Complete H/D equilibration would have given a d_0:d_1:d_2:d_3:d_4:d_5:d_6:d_7 ratio of 2:3:4:7:10:15:24:35.

Similar addition of CH_3CH_2CN (3.0 equiv) to a −78 °C THF solution of carbanion **5** gave, as assayed after 2 h by ^{31}P NMR spectroscopy, a (60 ± 5):(40 ± 5) **5**:**2** mixture (Scheme III).[18] After 1 day, the **5**:**2** ratio was (40 ± 5):(60 ± 5). No further change occurred after another day at −78 °C. Hence, the C_α protons of **2** have a lower ion-pair acidity than those of CH_3CN ($pK_a(H_2O)$ = 31.5; pK_a(DMSO) = 31.3)[23] and an ion-pair acidity comparable to those of CH_3CH_2CN (pK_a(DMSO) = 32.5).[23a,24] If a pK_a(THF) of 32.5 is assumed for CH_3CH_2CN, these data give a pK_a(THF) of ca. 32 for the C_α protons of **2**. If a K_{eq} of ≥100 is then assumed for carbanions **5**/**6** (Scheme I), the cyclopentadienyl protons of **2** would have a pK_a(THF) of ≥34. In any event, the (η^5-C_5H_5)Re(NO)(PPh_3)– substituent is clearly carbanion *destabilizing* relative to a proton.

Scheme IV. Reactions of α-Cyanoethyl Complexes (*SR,RS*)-4 and (*SS,RR*)-4 with *n*-BuLi/TMEDA



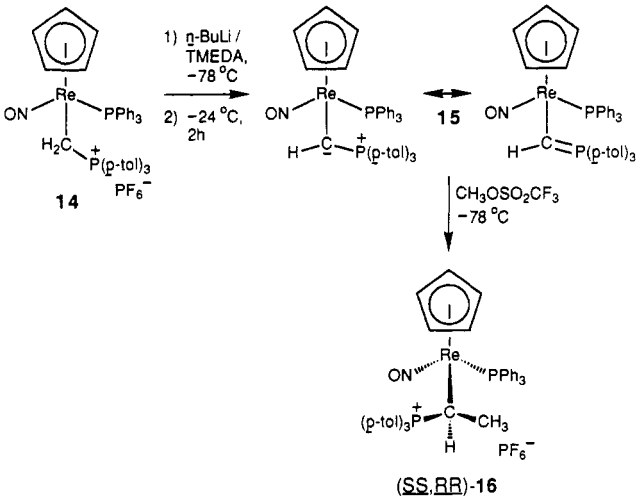
5. Deprotonation of Other Cyanoalkyl Complexes. The generation of carbanions from α-cyanoethyl complexes (*SR,RS*)/(*SS,RR*)-**4** was attempted next (Scheme IV). The reaction of (*SR,RS*)-**4** and *n*-BuLi/TMEDA in THF at −78 °C was monitored by ^{31}P NMR spectroscopy. A new complex rapidly and quantitatively formed (24.8 ppm). On the basis of the 2.9 ppm downfield shift (see above), this resonance was attributed to the lithiocyclopentadienyl complex (*SR,RS*)-(η^5-C_5H_4Li)Re(NO)(PPh_3)(CH(CH_3)CN) ((*SR,RS*)-**10**). Accordingly, subsequent addition of CH_3OSO_2F gave the methylcyclopentadienyl complex (*SR,RS*)-(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(CH(CH_3)CN) ((*SR,RS*)-**11**) in 74% yield after workup. Similarly, reaction of (*SS,RR*)-**4** and *n*-BuLi/TMEDA cleanly gave (*SS,RR*)-(η^5-C_5H_4Li)Re(NO)(PPh_3)(CH(CH_3)CN) ((*SS,RR*)-**10**; ^{31}P NMR 24.7 ppm). Addition of $CH_3OSO_2CF_3$ yielded (*SS,RR*)-(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(CH(CH_3)CN) ((*SS,RR*)-**11**, 92%). Both (*SR,RS*)- and (*SS,RR*)-**11** exhibited ^1H and ^{13}C NMR resonance patterns characteristic of monosubstituted cyclopentadienyl ligands (Table I).[25]

(23) (a) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Mathews, W. S. *J. Org. Chem.* **1977**, *42*, 321. (b) Bordwell, F. G.; Fried, H. E. *Ibid.* **1981**, *46*, 4327 and references therein.

(24) (a) It should be emphasized that these experiments order "*ion pair*" acidities, since they involve equilibria between two acids and two (ion-paired) bases, as opposed to a simple proton ionization. (b) 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. (c) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

(25) (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.

Scheme V. Generation and Stereospecific Alkylation of the Rhenium-Substituted Ylide 15



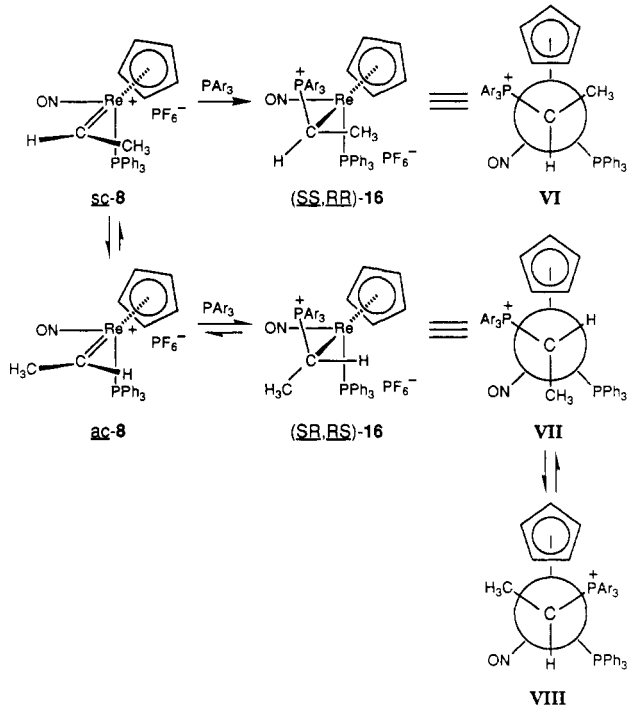
The lithiocyclopentadienyl complex (*SR,RS*)-**10** showed no decomposition over the course of 1.5 h at 0 °C. However, over the course of 3 h at −24 °C, (*SS,RR*)-**10** partially decomposed (ca. 15%) to a ca. 1:1:1 mixture of (*SS,RR*)-**4**, PPh_3 (−8.6 ppm), and a new complex with a plausible ^{31}P NMR chemical shift for a rhenium-substituted carbanion (32.0 ppm, broad). Additional time or warming gave a multitude of products. Thus, addition of an α-methyl substituent to **2** appears to significantly decrease the C_α proton acidity.

We sought to briefly investigate the possibility of generating carbanions at more remote positions on alkyl ligand side chains. Hence, "anion" **1** and $TsOCH_2CH_2CN$ were combined in THF at −78 °C (eq iii).[15] Preparative HPLC gave the β-cyanoalkyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CN)$ (**12**) in 40% yield. However, reactions of **12** and *n*-BuLi/TMEDA (or LDA) as above gave a multitude of deprotonation products, as assayed by ^{31}P NMR spectroscopy. One resonance suggested the presence of a lithiocyclopentadienyl complex. Upon methylation, several neutral complexes formed, including one containing a methylcyclopentadienyl ligand. However, we were unable to identify deprotonation/alkylation protocols that gave tractable product mixtures.

6. Synthesis and Reactivity of a Rhenium-Substituted Ylide. We have previously reported the preparation of the ylide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$ (**13**) from the methylidene complex **3** and PPh_3.[14] Complex **13** did not undergo well-defined reactions when treated with *n*-BuLi/TMEDA in THF. We thought that this might be due to its poor THF solubility—a property typical of cationic complexes in this series. Hence, the more soluble *p*-tolyl derivative $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-tol})_3)]^+PF_6^-$ (**14**, 98%) was analogously synthesized from **3** and $P(p\text{-tol})_3$. Spectroscopic data, including NMR spectra in $CDCl_3$, are summarized in Table I.

The reaction of **14** and *n*-BuLi/TMEDA in THF (Scheme V) was monitored by ^{31}P NMR spectroscopy over the temperature range −78 to −24 °C. Disappearance of **14** (39.2 d ppm, J_{PP} = 15.5 Hz, $P(p\text{-tol})_3$; 21.5 d ppm, J_{PP} = 15.6 Hz, PPh_3) was rapid at −78 °C. One major product (**15**) and several minor products formed. Over the course of 2 h at −24 °C, complete conversion to **15** occurred (30.3 d ppm, J_{PP} = 22.7 Hz; 15.2 d ppm, J_{PP} = 22.4 Hz). Subsequent methylation ($CH_3OSO_2CF_3$, −78 °C) gave the new ylide complex (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)P(p\text{-tol})_3)]^+PF_6^-$ ((*SS,RR*)-**16**) in 83% yield after workup. No trace of the opposite diastereomer (see below) was noted at −78 °C. The isolation of (*SS,RR*)-**16** as a PF_6^- salt (from the starting material **14**) as opposed to a $CF_3SO_3^-$ salt (from the methylating agent) was confirmed by an IR ν_{PF} band (839 cm^{-1}) and microanalysis. The intermediate **15** was in turn assigned as the rhenium-substituted ylide or "Wittig reagent" $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}P(p\text{-tol})_3)$.

Scheme VI. Reactions of the Ethylidene Complex 8 with $P(p\text{-tol})_3$ (PAr_3)



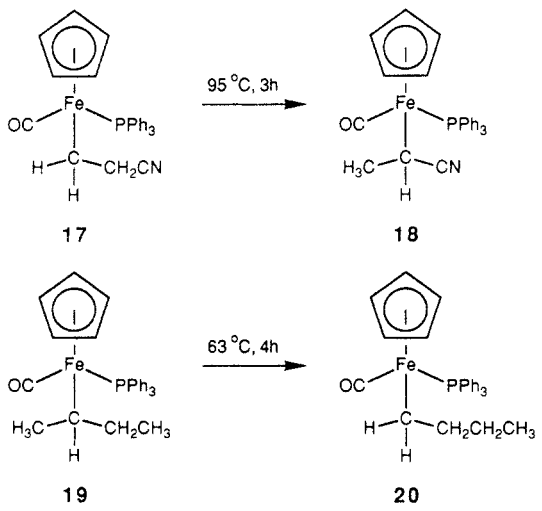
We sought to establish the stereochemistry of (*SS,RR*)-**16** via the same strategy used for the α-cyanoethyl complexes **4** above. Hence, the less stable ethylidene complex Re=C geometric isomer *sc*-**8** was treated with $P(p\text{-tol})_3$ at −78 °C (Scheme VI). Workup gave (*SS,RR*)-**16** (90%), which was identical with the product of Scheme V.

Surprisingly, reaction of the more stable ethylidene complex Re=C isomer *ac*-**8** with $P(p\text{-tol})_3$ also gave (*SS,RR*)-**16** upon workup! Hence, both processes were monitored by ^1H and ^{31}P NMR spectroscopy in CD_2Cl_2 at −78 °C. The reaction of *sc*-**8** and $P(p\text{-tol})_3$ cleanly gave (*SS,RR*)-**16** and was complete within 10 min. However, the reaction of *ac*-**8** and $P(p\text{-tol})_3$ (1.9 equiv) gave a *new* ylide complex with the following NMR properties: ^1H (δ) 3.46 br m (ReCH), 1.52 dd (J_{HH} = 6.0 Hz, J_{HP} = 21.6 Hz, $CHCH_3$); ^{31}P (ppm) 39.3 d (J_{PP} = 15.8 Hz, $P(p\text{-tol})_3$), 21.6 d (J_{PP} = 16.3 Hz, PPh_3). This compound was assigned as the opposite ylide complex diastereomer (*SR,RS*)-**16** (Scheme VI). The sample was warmed to room temperature, and isomerization to (*SS,RR*)-**16** commenced (data in the Experimental Section). After 2 days a (72 ± 2):(28 ± 2) (*SS,RR*)/(*SR,RS*)-**16** mixture was present. The rate of this isomerization would logically be dependent upon phosphine concentration. This would account, in part, for the exclusive isolation of (*SS,RR*)-**16** under preparative reaction conditions where phosphine is removed during workup.

Discussion

1. Chemistry of Cyanoalkyl Complexes. A surprisingly large number of (α-cyanoalkyl)metal complexes have been described in the literature.[26] Also, the polarity of

Scheme VII. Thermal Equilibration of Iron Alkyl Complexes



17 18 19 20

metal–carbon σ bonds ($M^{\delta+}$–$C^{\delta-}$) and the carbanion-stabilizing nature of α-cyano substituents[23,24b] are well established. Hence, α-cyanoalkyl complexes might be expected to exhibit enhanced thermodynamic stability relative to that of isomeric compounds. Accordingly, Reger has found that the primary (β-cyanoethyl)iron complex **17** cleanly isomerizes to the secondary α-cyanoethyl complex **18** (Scheme VII).[26c] Usually, secondary alkyl complexes are *less* stable than primary alkyl complexes, as illustrated by the isomerization of the *sec*-butyl iron complex **19** to the *n*-butyl complex **20** (Scheme VII).[27]

In the same vein, the polarity of a metal–carbon σ bond should destabilize a C_α carbanion. Furthermore, the rhenium fragment $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$– is a powerful π donor.[22,28] Accordingly, Scheme III shows that $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$– is a carbanion-*destabilizing* substituent relative to a proton. The magnitude of the effect (ca. 1 pK_a unit) is close to that of a methyl group. As expected, these σ/π donor properties also decrease the IR ν_{CN} values of α-cyanoalkyl complexes **2**, (*SR,RS*)/(*SS,RR*)-**4**, (*SR,RS*)/(*SS,RR*)-**7**, and (*SR,RS*)/(*SS,RR*)-**11** (2187–2197 cm^{-1}) relative to those of common organic nitriles (2275–2220 cm^{-1})[29] and β-cyanoethyl complex **12** (2233 cm^{-1}).

The pK_a(THF) of the cyclopentadienyl protons of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ has been shown to be ca. 35.9.[13,24] In **2**, the α-cyano substituent should render the cyclopentadienyl protons slightly more acidic. However, they remain at least 2 pK_a units *less* acidic than the C_α protons (pK_a ca. 32), as evidenced by the quantitative isomerization of lithiocyclopentadienyl complex **6** to the C_α carbanion **5** (Scheme I). Nonetheless, *n*-BuLi/TMEDA competitively abstracts the less acidic cyclopentadienyl protons of **2**.

This phenomenon has precedent. For example, reactions of the hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ and phenylacetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2C_6H_5)$ with *n*-BuLi/TMEDA both give exclusive cyclopentadienyl ligand deprotonation.[11,13] However, it can be shown that the hydride and phenylacetyl ligand protons are more acidic. This behavior is thought to be due to the substantial rehybridization and negative charge delocalization that must occur en route to the more stable anions. Thus, the full thermodynamic stability of the anions is not reflected until late in the reaction coordinate. In contrast, cyclopentadienyl ligand deprotonation does not entail rehybridization or charge delocalization. Hence, formation of a less stable anion can compete kinetically.[11,13]

The introduction of an α-methyl substituent to **2** should render the remaining C_α proton 1–2 pK_a units less acidic—but probably still more acidic than the cyclopentadienyl protons. However, Scheme IV shows that α-cyanoethyl complexes (*SR,RS*)/(*SS,RR*)-**4** undergo exclusive cyclopentadienyl ligand deprotonation to (*SR,RS*)/(*SR,RS*)-**10**. We provisionally attribute this to a kinetic effect. However, efforts to equilibrate (*SR,RS*)/(*SS,RR*)-**10** to presumably more stable C_α carbanions were complicated by independent thermal decomposition.

The diastereotopic C_α protons of **2** should in principle exhibit different kinetic acidities. There is abundant precedent for the stereospecific abstraction of one of two diastereotopic protons in chiral molecules.[30] Also, only one of the two diastereotopic C_α hydrides in alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ is abstracted by $Ph_3C^+X^-$ in the generation of alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+X^-$.[22] However, our inability to prepare diastereomerically pure samples of **2**-d_1 precluded any probes for such behavior.

2. Related Transition-Metal/Carbanion Chemistry. The C_α deprotonation of neutral metal alkyl complexes appears to have little precedent. For example, Magnus has reported the deprotonation of what would be conventionally regarded as an alkyne complex, (trimethylsilyl)-acetylene-derived **21**, to carbanion **22** (eq iv).[3b] Collum has found that the 16-valence-electron palladium complex **23** and $K^+t\text{-}BuO^-$ react to give the Wittig reagent **25** (eq v).[3c] He proposes the intermediacy of C_α enolate anion **24** but also recognizes that formulations with a $^-Pd{=}C$ double bond are possible.[6] Attempts to deprotonate the neutral, 18-valence-electron complex $(\eta^5\text{-}C_5R_5)W(CO)_3(CH_2SOC_6H_5)$ were unsuccessful, despite the presence of a C_α activating group.[3d]

Bickelhaupt has reported that $(\eta^5\text{-}C_5H_5)_2TiCl_2$ reacts with 2 equiv of the 1,3-di-Grignard reagent $CH_2(MgBr)_2$ to give the bis(carbanion) $(\eta^5\text{-}C_5H_5)_2Ti(CH_2MgBr)_2$ (**27**, eq vi).[3a] This most unusual, formally 16-valence-electron complex was isolated as a red precipitate and characterized by chemical reactions. No spectroscopic or structural data are yet available to help evaluate the bonding in **27**. In principle, the titanium could acquire an 18-valence-electron count by a Ti=C double bond to one C_α or an intermediate Ti⁻⁻C bond to both C_α. Regardless, **27** is the closest approximation to a carbanion attached to a coordinatively saturated metal fragment isolated to date.

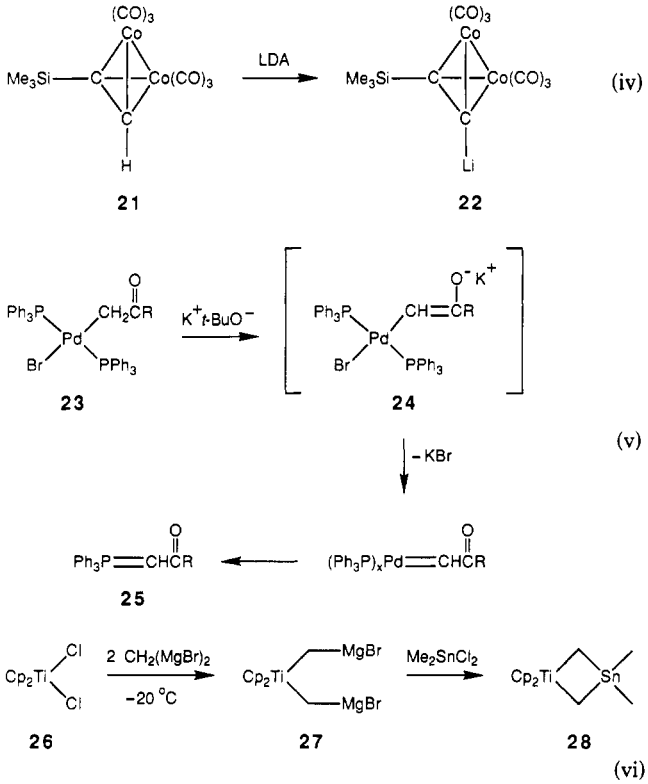
(26) Selected references: (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Treichel, P. M.; Firsich, D. W.; Lemmen, T. H. *J. Organomet. Chem.* **1980**, *202*, C77. (c) Reger, D. L.; McElligott, P. *Ibid.* **1981**, *216*, C12. (d) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *Ibid.* **1983**, *246*, 325. (e) Kubicki, M. M.; Kergoat, R.; Gomes de Lima, L. C.; Cariou, M.; Scordia, H.; Guerchois, J. E.; L'Haridon, P. *Inorg. Chim. Acta* **1985**, *104*, 191. (f) Porta, F.; Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1990**, *9*, 929. (g) Ko, J. J.; Bockman, T. M.; Kochi, J. K. *Ibid.* **1990**, *9*, 1833.

(27) (a) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104. (b) See also: Bennet, M. A.; Crisp, G. T. *Organometallics* **1986**, *5*, 1792, 1800.

(28) (a) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (b) 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. (c) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(29) (a) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1981; p 499. (b) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Franscico, CA, 1962; pp 63–64.

(30) (a) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; pp 36–90. (b) Wolfe, S. In *Studies in Organic Chemistry*; Bernardi, F., Csizmadia, S. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Vol. 19, pp 133–190.

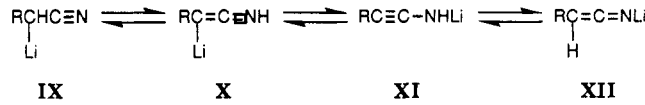


3. Structure of Carbanion 5. The rhenium-substituted carbanion **5** presents several structural issues. First, are any alternative formulations with a $^{-}$Re=CHCN double bond consistent with the data? This would place 20 valence electrons on rhenium, unless cyclopentadienyl ligand slippage[31] or nitrosyl ligand bending[32] is invoked.

We have considered the possibility of nitrosyl ligand bending in **5** in some detail. This should greatly decrease the IR ν_{NO} value.[32] Indeed, the ν_{NO} of **5** (Figure 1, 1597 cm^{-1}) is the lowest observed to date in (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes. However, phosphido complexes (η^5-C_5H_5)Re(NO)(PPh_3)($\ddot{P}R_2$), which also bear lone electron pairs α to rhenium, exhibit ν_{NO} as low as 1635 cm^{-1}.[28c] Crystal structures confirm the presence of linear nitrosyl ligands in these compounds. Similarly, amide complexes (η^5-C_5H_5)Re(NO)(PPh_3)($\ddot{N}R_2$) exhibit ν_{NO} as low as 1624 cm^{-1}.[33] The rhenium-centered anion Li^{+}[(η^5-C_5H_5)Re(NO)(PPh_3)]$^{-}$ (**1**), which requires a linear nitrosyl ligand to maintain 18 valence electrons, exhibits ν_{NO} at 1612–1597 cm^{-1}, depending upon ion pairing.[13]

The ruthenium dinitrosyl complex [$RuCl(NO)_2(PPh_3)_2$]$^{+}PF_6^{-}$ contains both linear and bent nitrosyl ligands.[32a] These exhibit ν_{NO} bands at 1845 and 1687 cm^{-1}, respectively. In view of this large difference, and the relatively small differences noted above, we formulate **5** as a linear nitrosyl complex. Also, we have found that amide complexes (η^5-C_5H_5)Re(NO)(PPh_3)($\ddot{N}R_2$) extrude PPh_3 at 40–60 °C to give reactive intermediates that contain a three-electron-donor amide ligand, (η^5-C_5H_5)Re(NO)(=NR_2).[34] This suggests that any isomerization of **5** to a $^{-}$Re=CHCN species would be accompanied by PPh_3 loss, as opposed to nitrosyl ligand bending or cyclopentadienyl ligand slippage.

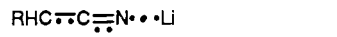
Scheme VIII. Possible Tautomeric Forms of Lithiated Nitriles



The deprotonated ligand in **5** can in principle exist in several tautomeric forms (IX–XII, Scheme VIII). The structures of lithiated organic nitriles have been studied in detail,[35,36] and IR ν_{CN} bands have been utilized to probe these possibilities. For example, the ν_{CN} values of Li(C_3H_3)$_2$CCN (2000 cm^{-1}), Li($(CH_3)_3Si$)$_2$CCN (2000 cm^{-1}), $LiCH_2CN$ (2160 cm^{-1}), and Li(C_6H_5)CHCN (2180 cm^{-1}) are considered too high to be consistent with XI or ketenimine-type tautomers X and XII.[35] Also, IR ν_{CLi} bands have been assigned in $^{6}LiCH_2CN$, $^{7}LiCH_2CN$, and $^{7}LiCD_2CN$.[35b] Thus, tautomers of the type IX have often been proposed to dominate.

The IR ν_{CN} of **5** is 1980 cm^{-1}, 219 cm^{-1} lower than that of precursor **2**. This suggests a tautomer analogous to those of the lithiated nitriles above. Also, the ν_{CN} of **5** is more intense than the ν_{NO} (Figure 1), opposite to the intensity order in **2** (starred peaks, Figure 1). The intensities of the ν_{CN} of aliphatic nitriles are strongly influenced by C_α substituents.[29] Electron-withdrawing groups (e.g., Cl) decrease intensities, whereas electron-donating groups (e.g., NH_2) increase intensities and bandwidths. Hence, a more intense ν_{CN} would be expected for a type IX tautomer.

Several structural properties of **5** cannot at this time be rigorously addressed. First, there are questions of C_α geometry and Re–C_α conformation. Here, there may be analogy to phosphido complexes (η^5-C_5H_5)Re(NO)-(PPh_3)($\ddot{P}RR'$), which contain a pyramidal phosphorus.[28c] Second, Boche and co-workers have recently determined the crystal structures of several lithiated nitrile/Lewis base adducts.[36] Except for a cyanocyclopropane derivative, these exhibit solid-state structures that are best formulated as



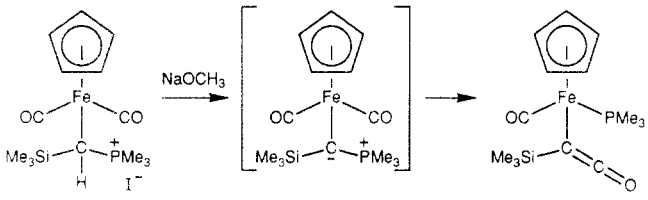
with carbon–nitrogen bond lengths close to those of normal nitriles. Thus, tautomer energies may be closely spaced, and any ground-state structure assigned to **5** need not be the species that is kinetically most reactive toward alkylating agents.

4. Deprotonation of Ylide Complex 14 and Related Compounds. The deprotonation of the cationic phosphorus ylide complex **14** (Scheme V) mirrors that of the neutral α-cyanomethyl complex **2** in several aspects. First, the rates are comparable. Second, more than one deprotonation product appears to initially form. Third, equilibration of the deprotonation products occurs upon warming. By analogy to organic phosphorus ylides,[37] the resulting rhenium-substituted ylide[9] **15** should exhibit a planar, sp^2-hybridized C_α carbon.

The chemistry of cationic phosphorus ylide complexes has been extensively studied.[8] However, reactions with bases are virtually unexplored. Malisch has described the reaction of the coordinatively saturated iron complex

(31) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.
(32) (a) Pierpont, C. G.; Van Derveer, D. G.; Durland, W.; Eisenberg, R. *J. Am. Chem. Soc.* **1970**, *92*, 4760. (b) Brock, C. P.; Collman, J. P.; Dolcetti, G.; Farnham, P. H.; Ibers, J. A.; Lester, J. E.; Reed, C. A. *Inorg. Chem.* **1973**, *12*, 1304. (c) Bottomley, F.; Darkwa, J.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1982**, 1039. (d) Feltham, R. D.; Enemark, J. H. *Top. Stereochem.* **1981**, *12*, 155.
(33) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349.
(34) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.
(35) (a) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1971**, *93*, 1714. (b) Das, R.; Wilkie, C. A. *Ibid.* **1972**, *94*, 4555. (c) See also: Arseniyadis, S.; Kyler, K. S.; Watt, D. S. *Org. React.* **1984**, *31*, 1.
(36) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277.
(37) (a) Hoffmann, R.; Boyd, B. B.; Goldberg, S. Z. *J. Am. Chem. Soc.* **1970**, *92*, 3929. (b) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon: New York, 1979; Vol. 3, pp 1312–1313.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH(SiMe_3)(PMe_3))]^+I^-$ (**29**) with $NaOCH_3$ (eq vii).[38] He proposes the initial formation of ylide

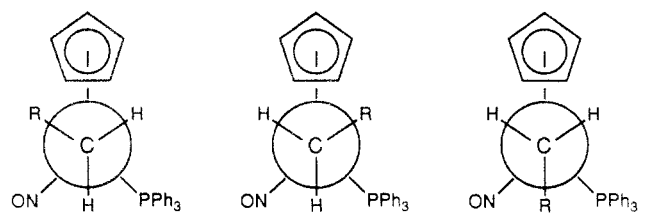


(vii)

intermediate **30**. However, rapid intramolecular rearrangement ensues to give ketenyl complex **31**.

A number of coordinatively *un*saturated, early-transition-metal- and actinide-substituted ylides of the formula $L_nM{-}CH{=}PR_3$ have been reported in the literature.[10] In most cases, these have been prepared by reaction of a metal precursor with an excess of the Wittig reagent $H_2C{=}PR_3$. Cationic ylide complexes $[L_nM{-}CH_2{-}PR_3]^+$ are believed to form initially and undergo subsequent deprotonation by the Wittig reagent. Since the ylide products are coordinatively unsaturated, resonance forms of the type $L_nM{=}CH{-}PAr_3$ are possible. Several crystal structures have been executed and confirm considerable metal–carbon double-bond character.[10a,c-f] Hence, these complexes are not good structural models for the rhenium-substituted ylide **15**.

5. Independent Syntheses of Alkylation Products. Before analyzing the stereochemistry of alkylation of C_α carbanion **5** and ylide **15**, it is helpful to interpret some unusual aspects of the independent synthesis of alkylation products (*SR,RS*)/(*SS,RR*)-**4** and (*SS,RR*)/(*SR,RS*)-**16** (Schemes II and VI). First, note that alkyl complexes such as **2** and **12**, which bear *one* C_α substituent, can in principle exist as three types of "staggered" $Re{-}C_\alpha$ rotamers: XIII, XIV, and XV. It is intuitive that rotamers of the type



XIII **XIV** **XV**

XIII, in which the C_α substituent occupies the region of space between the small nitrosyl and medium-sized cyclopentadienyl ligands, should be the most stable.[39] Several studies have shown that type XV rotamers, in which the C_α substituent resides between the nitrosyl and bulky PPh_3 ligands, are the least stable.[28a,40,41] This interstice is much smaller, as expected from the ca. 90° ON–Re–PPh_3 bond angles.[22a,28]

Next, consider an alkyl complex with three sterically differentiated C_α substituents, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$(CLMS). Since C_α is a chiral center, two diastereomers can exist. For one diastereomer, a $Re{-}C_\alpha$ rotamer will be possible in which the large group L resides between the nitrosyl and cyclopentadienyl ligands and the small group S resides between the nitrosyl and PPh_3 ligands. This will be the most stable of the three $Re{-}C_\alpha$ rotamers. However, in the other diastereomer, an analogous steric "fit" is not obtainable in any $Re{-}C_\alpha$ rotamer. Consequently, this diastereomer should be less stable.

This conformational analysis rationalizes the diastereomer stability order observed for ylide complexes **16** (*SS,RR* > *SR,RS*, Scheme VI). Diastereomer (*SS,RR*)-**16** can exist as $Re{-}C_\alpha$ rotamer VI, in which the very large PAr_3 substituent resides between the nitrosyl and cyclopentadienyl ligands and the small hydrogen substituent resides between the nitrosyl and PPh_3 ligands. However, a mismatch is found in all $Re{-}C_\alpha$ rotamers of (*SR,RS*)-**16**: VII places the medium-sized methyl group between the nitrosyl and PPh_3 ligands, VIII places the large PAr_3 group between the cyclopentadienyl and PPh_3 ligands, and the third rotamer (not shown) places the large PAr_3 group between the nitrosyl and PPh_3 ligands.

The preceding analysis can be extended to predict diastereomer stabilities for a variety of formally octahedral $(\eta^5\text{-}C_5H_5)M(X)(Y)$(CLMS) complexes. Indeed, a related isomerization of diastereomeric $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$(CLMS) complexes has been similarly rationalized.[42]

Consider next the relative *rates* of nucleophile additions to C_α of ethylidene complexes *sc*-**8** and *ac*-**8**. For example, PAr_3 attack upon *sc*-**8** forces the methyl group into the medium-sized interstice between the cyclopentadienyl and PPh_3 ligands (Scheme VI). This gives the most stable $Re{-}C_\alpha$ rotamer, VI, of the more stable ylide complex diastereomer, (*SS,RR*)-**16**. Analogous PAr_3 attack upon *ac*-**8** forces a methyl group into the small interstice between the nitrosyl and PPh_3 ligands, giving rotamer VII of the less stable diastereomer (*SR,RS*)-**16**. Intuitively, a faster rate would be expected in the former addition.

The PAr_3 addition reactions in Scheme VI are both rapid at −78 °C. However, the cyanide addition reactions in Scheme II show dramatic rate differences. Whereas ethylidene complex *sc*-**8** smoothly adds cyanide at −78 °C, *ac*-**8** remains unreacted in refluxing dichloromethane. The corresponding addition product, (*SR,RS*)-**4**, is independently available from carbanion **5** and does not revert to cyanide and *ac*-**8** under a variety of conditions. Thus, the lower reactivity of *ac*-**8** does not likely arise from unfavorable thermodynamics. Since the incoming cyanide C_α substituent is similar in size to the methyl C_α substituent, Scheme II differs subtly from Scheme VI. However, the key point is that cyanide addition to *ac*-**8** forces a methyl group into the congested region between the nitrosyl and PPh_3 ligands (to give a rotamer IV that should be less stable than alternative V), whereas addition to *sc*-**8** fits a small hydrogen into this region (to give the most stable $Re{-}C_\alpha$ rotamer II).

Finally, attention should be drawn to elegant recent work of Brookhart, Liu, and Buck.[43] These researchers have studied the addition of a variety of nucleophiles to iron alkylidene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)(=CHR')]^+CF_3SO_3^-$ (R = CH_3, CH_2CH_3, C_6H_5; R′ = CH_3, C_6H_5). A large body of quantitative rate and product distribution data show that *sc* Fe=C isomers are distinctly more reactive than *ac* Fe=C isomers. The preceding ra-

(38) Voran, S.; Malisch, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 151.

(39) By criteria detailed elsewhere (Bodner, G. S.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Organometallics* **1989**, *8*, 2399), the δ 1.93 ^1H NMR resonance of cyanomethyl complex **2** can be assigned to the proton that resides between the cyclopentadienyl and PPh_3 ligands in rotamer XIII, and the δ 2.55 resonance can be assigned to the proton that resides between the nitrosyl and PPh_3 ligands.

(40) (a) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711. (b) Seeman, J. I.; Davies, S. G. *Ibid.* **1985**, *107*, 6522.

(41) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481.

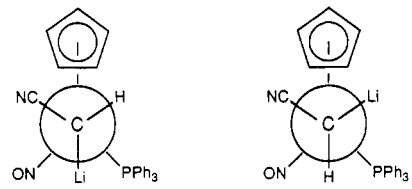
(42) Ayscough, A. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1648.

(43) (a) Brookhart, M.; Liu, Y.; Buck, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2337. (b) Liu, Y. Ph.D. Thesis, The University of North Carolina at Chapel Hill, 1989.

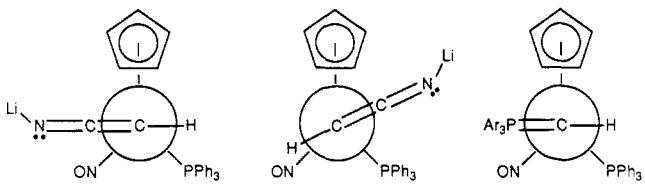
tionale of our data borrows heavily from their analysis.

5. Stereochemistry of Alkylation. Schemes I and V show that C_α carbanion **5** and ylide **15** alkylate with *opposite* stereochemistry. Accordingly, we have sought to formulate transition-state models that rationalize each result.

First, consider the possibility that **5** undergoes alkylation via a tautomer of the type IX (Scheme VIII). Two Re/C_α diastereomers are possible (*SR,RS* and *SS,RR*), as depicted in arbitrary Re–C_α rotamers XVI and XVII. We presume



XVI (SR,RS) XVII (SS,RR)



XVIII XIX XX

that such diastereomers would readily interconvert, analogously to diastereomers of phosphido and amide complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(ẊRR′),[28c,34,35] and that alkylation could in principle occur via any Re–C_α rotamer. The direct replacement of the C_α lithium in XVI (or a rotamer) by an alkyl group would give the correct product stereochemistry. Conversely, replacement of the lithium in XVII by an alkyl group would give the *in*correct product stereochemistry. However, we are presently unable to identify any feature that would render the *SR,RS* diastereomer far more reactive.

Next, consider the possibility that **5** reacts via a tautomer of the type XII. On the basis of the steric considerations detailed above, and precedent with the vinyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(CX=CHR),[44] XVIII would be a plausible choice for the reactive Re–C_α rotamer. An alkylating agent would be expected to attack C_α of XVIII from a direction anti to the PPh$_3$ ligand.[22,24] However, this would *not* give the correct product stereochemistry. Alternatively, the Re–C_α bond in XVIII could be rotated clockwise by ca. 150° to give XIX. Now, analogous alkylation would give the correct product stereochemistry. However, we are presently unable to offer a compelling reason why XVIII should be far less reactive than XIX (although we do note that alkylation of XVIII should force the cyanide substituent toward the congested nitrosyl/PPh$_3$ interstice). Thus, models that are good starting points for rationalizing stereospecific reactions of other (η^5-C_5H_5)Re(NO)(PPh$_3$)(X) complexes do not seem to offer insight into the stereospecific alkylation of **5**. Hence, this phenomenon remains an interesting and attractive problem for future experimental and theoretical research.

In contrast, a simple model accounts for the stereochemistry of alkylation of ylide **15**. As a consequence of the bulky PAr$_3$ moiety, Re–C_α rotamer XX would be expected to dominate. In this case, C_α alkylation from a direction anti to the PPh$_3$ ligand would give the correct product stereochemistry.

7. Summary. We have described the first C_α deprotonation of a neutral, coordinatively saturated metal alkyl complex to an observable carbanion and the first C_α deprotonation of a cationic, coordinatively saturated ylide complex to an observable neutral ylide. Carbanion-stabilizing C_α substituents are required to offset the destabilizing effect of the metal. When the metal fragment is chiral, such carbanions and ylides can undergo alkylation with extremely high diastereoselectivity. Precursor **3** of the alkyl and ylide complexes is available in optically active form.[45] Hence, these reactions have the potential to be used in the synthesis of optically active organic molecules.

Experimental Section

General Considerations. 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 (^{1}H, ^{13}C) and FT-80A (^{31}P) spectrometers as outlined in Table I. Mass spectra were obtained on a VG 770 spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories.

Solvents were purified as follows: THF, ether, and benzene, distilled from Na/benzophenone; hexane, heptane, and toluene, distilled from Na; acetone, distilled from $CaSO_4$; CH_2Cl_2 and $CHCl_3$, distilled from P_2O_5; ethyl acetate, used as received; CD_2Cl_2, vacuum-transferred from CaH_2.

Reagents were obtained or purified as follows: $Ph_3C^+PF_6^-$ (Columbia, Aldrich), recrystallized (CH_2Cl_2/benzene) under N_2 and stored under N_2, −25 °C; P(*p*-tol)$_3$, prepared from PCl_3 (MCB) and $BrMgC_6H_4CH_3$;[46] CF_3COOD, prepared as described previously;[44] $CH_3OSO_2CF_3$ and TMEDA (Aldrich), distilled from CaH_2; CH_3CN (Fisher), CD_3CN (Stohler), CH_3CH_2CN (Aldrich), and $ClCH_2CN$ (MCB), distilled from CaH_2 and stored over $CaSO_4$; *n*-C_4H_9I (Aldrich), distilled from $MgSO_4$; $TsOCH_2CH_2CN$, obtained by a literature procedure;[47] *n*-BuLi (Aldrich), standardized[48] before use; PPN^+CN^-, prepared from PPN^+Cl^- (Aldrich) and KCN (Baker).[49]

$PPN^+PF_6^-$. A Schlenk flask was charged with $Ag^+PF_6^-$ (0.27 g, 0.47 mmol, Aldrich), acetone (50 mL), and a stirbar. Then PPN^+Cl^- (0.12 g, 0.48 mmol) was added, and the mixture was stirred for 5 h and (in a glovebox) filtered. Solvent was removed from the filtrate by rotary evaporation. The resulting white solid was extracted with CH_2Cl_2. The extract was filtered, and the filtrate was concentrated to ca. 15 mL. Ether was slowly added by vapor diffusion. Large white crystals of $PPN^+PF_6^-$·0.75CH_2Cl_2 formed, which were collected and dried in vacuo (0.24 g, 0.35 mmol, 75%). ^{31}P NMR (ppm, CH_2Cl_2): 21.0 s, PPN^+; −144.9 sept, J_{PF} = 711 Hz, PF_6^-. ^{1}H NMR (δ, acetone-d_6): 7.76–7.53 m, 30 H; 5.62 s, 0.75 CH_2Cl_2. Anal. Calcd for $C_{36}H_{30}F_6NP_3$·0.75CH_2Cl_2: C, 59.07; H, 4.25. Found, C, 58.99; H, 4.42.

Preparation of (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CN) (2). A. A Schlenk tube was charged with (η^5-C_5H_5)Re(NO)(PPh$_3$)(H) (0.41 g, 0.71 mmol),[13] THF (20 mL), and a stirbar. The yellow solution was cooled to −15 °C and stirred. Then TMEDA (0.11 g, 0.92 mmol) and *n*-BuLi (0.35 mL, 2.4 M in hexane) were added, and the solution turned dark red. After 0.5 h, the solution was cooled to −78 °C, and $ClCH_2CN$ (0.23 g, 3.0 mmol) was added. After 0.5 h, the resulting dark orange solution was transferred to a round-bottom flask, and solvents were removed by rotary evaporation. The residue was extracted with CH_2Cl_2. 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/

(44) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Chem. Soc.* **1987**, *109*, 7688.

(45) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

(46) Mann, F. G.; Chaplin, E. J. *J. Chem. Soc.* **1937**, 527.

(47) Marshall, D. R.; Thomas, P. S.; Stirling, J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1914.

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

(49) Martinsen, A.; Songstad, J. *Acta Chem. Scand.* **1977**, *31*, 645.

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 −24 °C for 2 days. The resulting orange crystals were collected by filtration and dried in vacuo at 57 °C to give **2** (0.28 g, 0.48 mmol, 68%), mp 168–169 °C. Anal. Calcd for $C_{25}H_{22}N_2OPRe$: C, 51.48; H, 3.80. Found: C, 51.52; H, 3.77.

B. A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.46 g, 0.83 mmol),[14] CH_2Cl_2 (40 mL), and a stirbar. The orange solution was cooled to −78 °C and stirred. Then $Ph_3C^+PF_6^-$ (0.38 g, 0.90 mmol) was added, and the solution turned yellow.[45] After 0.5 h, PPN^+CN^- (0.50 g, 0.90 mmol) was added. After 1.5 h, the resulting orange solution was transferred to a round-bottom flask, and solvent was removed by rotary evaporation. Chromatography and crystallization as above gave **2** (0.43 g, 0.73 mmol, 88%), mp 168–169 °C.

Preparation of (*SR,RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CN)$ ((*SR,RS*)-4). A Schlenk tube was charged with **2** (0.11 g, 0.19 mmol), THF (5 mL), and a stirbar. The orange solution was cooled to −78 °C and stirred. Then TMEDA (0.025 g, 0.21 mmol) and *n*-BuLi (0.080 mL, 2.5 M in hexane) were added and the solution turned dark orange. After 2.0 h, $CH_3OSO_2CF_3$ (0.13 g, 0.78 mmol) was added. After 10 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 1-cm plug of Celite, and solvent was removed by rotary evaporation. The resulting orange oil was chromatographed on a 12 × 2.5 cm silica gel column with 50:50 (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 (5 mL) and this solution layered with hexane and kept at −24 °C for 2 days. The resulting orange crystals were collected by filtration and dried in vacuo at 57 °C to give (*SR,RS*)-**4** (0.084 g, 0.14 mmol, 75%), mp 224–226 °C dec. Anal. Calcd for $C_{26}H_{24}N_2OPRe$: C, 52.25; H, 4.04. Found: C, 52.22; H, 3.87.

Preparation of (*SS,RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)CN)$ ((*SS,RR*)-4). This compound was prepared from $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ (0.37 g, 0.66 mmol),[22b] $Ph_3C^+PF_6^-$ (0.41 g, 0.75 mmol), and PPN^+CN^- (0.42 g, 0.75 mmol) in a procedure analogous to synthesis B of **2** (0.35 g, 0.60 mmol, 91%); mp 192–193 °C. Anal. Calcd for $C_{26}H_{24}N_2OPRe$: C, 52.25; H, 4.04. Found: C, 52.31; H, 4.03.

Preparation of (*SR,RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(n\text{-}C_4H_9)CN)$ ((*SR,RS*)-7). Complex **2** (0.056 g, 0.096 mmol), THF (3 mL), TMEDA (0.012 g, 0.11 mmol), and *n*-BuLi (0.045 mL, 2.5 M in hexane) were combined in a procedure analogous to that given for (*SR,RS*)-**4**. Then *n*-C_4H_9I (0.065 g, 0.35 mmol) was added. After 0.5 h, the resulting dark 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, and the solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was chromatographed on a 12 × 2.5 cm silica gel column with 20:80 (v/v) ethyl acetate/hexane. The yellow band was collected and concentrated to an oil by rotary evaporation. The oil was dissolved in toluene (3 mL), layered with heptane, and kept at −24 °C for 2 days. The resulting small orange crystals were collected by filtration and dried in vacuo at 57 °C to give (*SR,RS*)-**7** (0.033 g, 0.051 mmol, 53%), mp 114–116 °C. Anal. Calcd for $C_{29}H_{30}N_2OPRe$: C, 54.45; H, 4.73. Found: C, 54.61; H, 4.82.

Preparation of (*SS,RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(n\text{-}C_4H_9)CN)$ ((*SS,RR*)-7). The complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(n\text{-}C_5H_{11})$ (0.20 g, 0.33 mmol),[22b] CH_2Cl_2 (10 mL), $Ph_3C^+PF_6^-$ (0.14 g, 0.36 mmol), and PPN^+CN^- (0.25 g, 0.44 mmol) were combined in a procedure analogous to synthesis B of **2**. After 0.5 h, the resulting orange solution was transferred to a round-bottom flask, and solvent was removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered, and the solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was chromatographed on a 12 × 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 (5 mL), layered with heptane, and kept at −24 °C for 1 day. The resulting small orange crystals were collected by filtration and dried in vacuo at 57 °C to give (*SS,RR*)-**7** (0.15 g, 0.24 mmol, 72%), mp 216–218 °C. Anal. Calcd for $C_{29}H_{30}N_2OPRe$: C, 54.45; H, 4.73. Found: C, 54.02; H, 4.76.

Preparation of (*SR,RS*)-$(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(CH(CH_3)CN)$ ((*SR,RS*)-11). A Schlenk tube was charged with (*SR,RS*)-**4** (0.077 g, 0.13 mmol), THF (5 mL), and a stirbar. The solution was cooled to −78 °C and stirred. Then TMEDA (0.018 g, 0.16 mmol) and *n*-BuLi (0.075 mL, 2.5 M in hexane) were added. After 1.5 h, $CH_3OSO_2CF_3$ (0.087 g, 0.53 mmol) was added. 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 3-cm silica gel plug with 50:50 (v/v) ethyl acetate/hexane. The filtrate was concentrated to an orange oil by rotary evaporation. The oil was dissolved in CH_2Cl_2 (2 mL), layered with hexane, and kept at −24 °C for 3 days. The resulting orange crystals were collected by filtration and dried in vacuo at 57 °C to give (*SR,RS*)-**11** (0.058 g, 0.095 mmol, 74%), mp 195–196 °C. Anal. Calcd for $C_{27}H_{26}N_2OPRe$: C, 53.02; H, 4.28. Found: C, 52.85; H, 4.14.

Preparation of (*SS,RR*)-$(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(CH(CH_3)CN)$ ((*SS,RR*)-11). Complex (*SS,RR*)-**4** (0.050 g, 0.084 mmol), THF (2 mL), TMEDA (0.012 g, 0.11 mmol), *n*-BuLi (0.070 mL, 1.4 M in hexane), and $CH_3OSO_2CF_3$ (0.023 g, 0.14 mmol) were combined in a procedure analogous to that given for (*SR,RS*)-**11**. The reaction mixture 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 the solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was dissolved in toluene (1 mL) and this solution layered with hexane and kept at −24 °C for 1 day. The resulting small orange crystals were collected by filtration and dried in vacuo at 75 °C to give (*SS,RR*)-**11** (0.047 g, 0.077 mmol, 92%), mp 197–198 °C. Anal. Calcd for $C_{27}H_{26}N_2OPRe$: C, 53.02; H, 4.28. Found: C, 53.02; H, 4.41.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CN)$ (12). The complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (0.500 g, 0.919 mmol), *n*-BuLi (1.10 mL, 1.0 M in hexane), and $TsOCH_2CH_2CN$ (0.517 g, 2.30 mmol; in 1 mL of THF) were combined in a procedure analogous to synthesis A of **2**. Solvents were removed by rotary evaporation, and the brown residue was extracted with CH_2Cl_2. The extract was filtered through a 1-cm plug of silica, and solvent was removed from the filtrate by rotary evaporation. The residue was taken up in 75:25 (v/v) hexane/ethyl acetate and purified by preparative silica gel HPLC. Solvent was removed from the second product fractions to give **12** as an orange powder (0.225 g, 0.376 mmol, 40%), mp 177–180 °C. Anal. Calcd for $C_{26}H_{24}N_2OPRe$: C, 52.24; H, 4.05. Found: C, 51.94; H, 4.51.

Addition of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{C}HCN)]^-$ to CF_3COOD. Complex **2** (0.059 g, 0.10 mmol), THF (2.0 mL), TMEDA (0.015 g, 0.13 mmol), and *n*-BuLi (0.090 mL, 1.3 M in hexane) were combined as described in the preparation of (*SR,RS*)-**4**. The solution was stirred at −78 °C for 3 h and was then cooled to −98 °C. A separate Schlenk tube was charged with CF_3COOD (0.074 g, 0.64 mmol) and a stirbar and cooled to −24 °C. Then the solution of **5** was added via transfer needle with vigorous stirring over the course of 5 min. The product **2**-d_1 was isolated as described above for **2**. Integration of a ^1H NMR spectrum showed a (68 ± 2):(32 ± 2) mixture of **3**-d_1 diastereomers, with predominant deuterium incorporation into the upfield H_α.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-}tol)_3)]^+PF_6^-$ (14). The complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.64 g, 1.15 mmol), CH_2Cl_2 (50 mL), $Ph_3C^+PF_6^-$ (0.50 g, 1.29 mmol), and $P(p\text{-tol})_3$ (0.59 g, 1.94 mmol) were combined in a procedure analogous to synthesis B of **2**. After 1 h, the resulting orange solution was warmed to room temperature and solvent was removed in vacuo. The residue was washed with ether (3 × 25 mL). The resulting light orange powder was dried in vacuo at 75 °C to give **14** (1.15 g, 1.13 mmol, 98%). The powder was dissolved in acetone (15 mL), and ether was slowly added by vapor diffusion. This gave large orange crystals of **14** that were dried in vacuo, mp >230 °C. Anal. Calcd for $C_{45}H_{43}F_6NOP_3Re$: C, 53.68; H, 4.30. Found: C, 53.67; H, 4.69.

Preparation of (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)P(p\text{-tol})_3)]^+PF_6^-$ ((*SS,RR*)-16). A. A Schlenk tube was charged with **14** (0.082 g, 0.081 mmol), THF (5 mL), and a stirbar. The orange solution was cooled to −78 °C and stirred. Then

TMEDA (0.012 g, 0.099 mmol) and *n*-BuLi (0.072 mL, 1.3 M in hexane) were added. The solution turned red and after 15 min was transferred to a −24 °C bath and stirred for 2 h. The solution was then cooled to −78 °C, and $CH_3OSO_2CF_3$ (0.023 g, 0.14 mmol) was added. After 0.5 h, the resulting red-orange solution was transferred to a round-bottom flask. 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 red oil was dissolved in CH_2Cl_2 (ca. 2 mL), and ether was slowly added by vapor diffusion at −5 °C. After 3 days, the resulting red-brown crystals were collected and dried in vacuo at 75 °C to give (*SS,RR*)-**16** (0.069 g, 0.067 mmol, 83%), mp 146–148 °C. Anal. Calcd for $C_{46}H_{45}F_6NOP_3Re$: C, 54.11; H, 4.45. Found: C, 53.79; H, 4.75.

B. The complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) (0.097 g, 0.17 mmol), CH_2Cl_2 (10 mL), $Ph_3C^+PF_6^-$ (0.079 g, 0.20 mmol), and P(*p*-tol)$_3$ (0.16 g, 0.53 mmol) were combined in a procedure analogous to synthesis B of **2**. After 1.5 h, the solution was warmed to room temperature and solvent was removed in vacuo. The residue was extracted with $CHCl_3$. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting orange solid was washed with ether (3 × 20 mL). The light orange powder was collected and dried in vacuo at 75 °C to give (*SS,RR*)-**16** (0.16 g, 0.15 mmol, 90%), mp 143–146 °C. Anal. Found: C, 54.05; H, 4.92.

Monitoring of Reactions by NMR Spectroscopy. The following experiments are representative.

(A) Carbanion Generation and Methylation. A 5-mm NMR tube was charged with **2** (0.040 g, 0.073 mmol) and THF (0.070 mL) and capped with a septum. A ^{31}P NMR spectrum of the orange solution was recorded at −78 °C (22.0 ppm, s). Then TMEDA (0.0093 g, 0.080 mmol) and *n*-BuLi (0.030 mL, 2.5 M in hexane) were added (−78 °C). The tube was shaken, and the solution became dark orange. After 5 min, a ^{31}P NMR spectrum was recorded (ppm, −78 °C: 25.3 sh, ca. 35%, **6**; 32.4 br, ca. 65%, **5**). The probe was warmed to −50 °C. After 1 h, a ^{31}P NMR spectrum was recorded (ppm: 25.0 sh, ca. 25%; 32.3 br, ca. 75%). The probe was warmed to −18 °C. After 10 min, a ^{31}P NMR spectrum was recorded (ppm: 24.7, ca. 5%; 32.1, ca. 95%; much sharper than at −50 °C). The dark yellow-orange solution was immersed in a −78 °C bath, and $CH_3OSO_2CF_3$ (0.038 g, 0.23 mmol) was added. The tube was shaken, and the solution became bright orange. After 5 min, a ^{31}P NMR spectrum was recorded (ppm, −18 °C: 22.2 sh, (*SR,RS*)-**4**).

(B) Addition of $CH_3OSO_2CF_3$ to a Mixture of 5 and 6. A 5-mm NMR tube was charged with **2** (0.010 g, 0.017 mmol) and THF (0.35 mL), capped with a septum, and immersed in a −78 °C bath. Then TMEDA (0.0031 g, 0.027 mmol) and *n*-BuLi (0.015 mL, 1.3 M in hexane) were added and the tube was shaken. After 5 min, a ^{31}P NMR spectrum was recorded (ppm, −78 °C: 25.9 sh, ca. 40%, **6**; 32.3 br, ca. 60%, **5**). Then $CH_3OSO_2CF_3$ (0.0015 g, 0.088 mmol) was added (−78 °C) and the tube was shaken. Within 5 min, a ^{31}P NMR spectrum was recorded (ppm: 32.1 sh, ca. 50%, **5**; 22.3 sh, ca. 50%, (*SR,RS*)-**4**).

(C) Ylide Generation and Methylation. A 5-mm NMR tube was charged with **14** (0.030 g, 0.030 mmol) and THF (0.60 mL) and capped with a septum. A ^{31}P NMR spectrum of the orange solution was recorded at −78 °C (ppm: 39.2 d, J_{PP} = 15.5 Hz, P(*p*-tol)$_3$; 21.5 d, J_{PP} = 15.6 Hz, PPh_3). Then TMEDA (0.0046 g, 0.040 mmol) and *n*-BuLi (0.028 mL, 1.3 M in hexane) were added (−78 °C). The tube was shaken, and the solution became dark red. After 5 min, a ^{31}P NMR spectrum was recorded at −78 °C (ppm: 30.3 d, J_{PP} = 22.7 Hz, P(*p*-tol)$_3$; 16.0 d, J_{PP} = 22.5 Hz, PPh_3, ca. 50%; minor peaks 31.7 d, J_{PP} = 16.5 Hz, 27.2 d, J_{PP} = 4.9 Hz, 24.2 d, J_{PP} = 15.7 Hz). The probe was warmed to −25 °C. After 3 h, a ^{31}P NMR spectrum was recorded (ppm: 30.4 d, J_{PP} = 22.5 Hz, P(*p*-tol)$_3$; 16.1 d, J_{PP} = 22.5 Hz, PPh_3). The tube was immersed in a −78 °C bath, and $CH_3OSO_2CF_3$ (0.013 g, 0.080 mmol) was added. The tube was shaken, and the solution became bright orange. After 15 min, a ^{31}P NMR spectrum was recorded (ppm, −24 °C: 42.1 d, J_{PP} = 17.4 Hz, P(*p*-tol)$_3$; 20.5 d, J_{PP} = 17.1 Hz, PPh_3, (*SS,RR*)-**16**).

(D) Reaction of *sc*-8 and P(*p*-tol)$_3$. A 5-mm NMR tube was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) (0.019 g, 0.034 mmol) and CD_2Cl_2 (0.50 mL) and capped with a septum. Another NMR tube was similarly charged with $Ph_3C^+PF_6^-$ (0.016 g, 0.042 mmol). The tubes were immersed in a −78 °C bath, and the contents of the first were added to the second via transfer needle. The tube was shaken to give a yellow solution of *sc*-**8** and kept at −78 °C for 45 min. Another NMR tube was similarly charged with P(*p*-tol)$_3$ (0.016 g, 0.053 mmol) and cooled to −78 °C. The solution of *sc*-**8** was added to the phosphine via transfer needle. The mixture was shaken and after 5 min became orange. NMR spectra were then recorded at −78 °C (^1H (δ) 3.68 br s (ReCH), 1.25 br d (J_{HP} = 20.2 Hz, ReCHCH_3); ^{31}P (ppm) 42.8 d (J_{PP} = 15.9 Hz), 19.7 d (J_{PP} = 16.8 Hz)) and showed complete formation of (*SS,RR*)-**16**. The tube was kept at room temperature for 1 day. A ^1H NMR spectrum was recorded (δ, 20 °C: 3.82 apparent sept, J = 7 Hz, ReCH; 1.40 dd, J_{HH} = 7.5 Hz, J_{HP} = 21.7 Hz, ReCHCH_3). The tube was kept at room temperature for another day, and the ^1H and ^{31}P NMR spectra remained unchanged.

(E) Reaction of *ac*-8 and P(*p*-tol)$_3$. The complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) (0.018 g, 0.032 mmol), CD_2Cl_2 (0.50 mL), and $Ph_3C^+PF_6^-$ (0.015 g, 0.038 mmol) were combined as described in the previous experiment. The resulting yellow solution was kept at room temperature for 3 h to generate a *ac*/*sc*-**8** equilibrium mixture and was then cooled to −78 °C. Another NMR tube was charged with P(*p*-tol)$_3$ (0.018 g, 0.060 mmol), capped with a septum, and cooled to −78 °C. The solution of **8** was added to the phosphine via transfer needle. The mixture was shaken and after 5 min became orange. NMR spectra were then recorded at −78 °C (^1H (δ) 3.46 br m (ReCH), 1.52 dd (J_{HH} = 6.0 Hz, J_{HP} = 21.6 Hz, ReCHCH_3, (*SR,RS*)-**16**), minor resonances of (*SS,RR*)-**16** at 3.63 and 1.20; ^{31}P (ppm) 39.3 d (J_{PP} = 15.8 Hz, P(*p*-tol)$_3$), 21.6 d (J_{PP} = 16.3 Hz, PPh_3)). The sample was kept at room temperature for 1 day. A ^1H NMR spectrum was recorded (δ, 20 °C: 3.82 br m, 34%; 3.58 br m, 66%; 1.69 dd, J_{HH} = 6.9 Hz, J_{HP} = 21.5 Hz, 66%; 1.39 dd, J_{HH} = 7.5 Hz, J_{HP} = 21.0 Hz, 34%). After an additional day, the δ 3.82/3.58 and δ 1.39/1.69 resonance ratios were (72 ± 2):(28 ± 2); chemical shifts and coupling constants were unchanged. A ^{31}P NMR spectrum showed resonances for (*SS,RR*)-**16** (ppm, 22 °C: 42.7 d, J_{PP} = 16.0 Hz; 19.7 d, J_{PP} = 15.9 Hz) in addition to those noted above.

Preparation of Deuterated Compounds. The key starting material (η^5-C_5D_5)Re(CO)$_3$ was prepared as previously described[11] and elaborated to **2**-d_5 by procedures noted above for undeuterated complexes. Complex **2**-d_2 was prepared from the deuteriomethylidene complex[45] [(η^5-C_5H_5)Re(NO)(PPh_3)(=CD_2)]$^+PF_6^-$ and PPN^+CN^-.

Labeling Experiments. The following experiments are representative, and others are detailed elsewhere.[50]

A. A Schlenk tube was charged with (η^5-C_5D_5)Re(NO)(PPh_3)(CH_2CN) (**2**-d_5; (86 ± 2):(14 ± 2) d_5/d_4; 0.020 g, 0.034 mmol), THF (0.30 mL), and a stirbar and was cooled to −78 °C. Then TMEDA (0.0050 g, 0.043 mmol) and *n*-BuLi (0.15 mL, 2.4 M in hexane) were added with stirring. After 2 h, $CH_3OSO_2CF_3$ (0.018 g, 0.11 mmol) was added. The product (*SR,RS*)-**4**-d_x was isolated as described for (*SR,RS*)-**4** above. The 70-eV mass spectrum of the product exhibited a *m/e* 600:601:602:603:604 intensity ratio of 42.3:58.9:72.6:100.0:22.9. Under identical conditions, the *m/e* 596:597:598:599:600 ratio for natural-abundance (*SR,RS*)-**4** was 55.0:17.3:100.0:25.6:4.9. These data indicate a (*SR,RS*)-**4**-d_5:(*SR,RS*)-**4**-d_4 ratio of (62 ± 2):(38 ± 2).

B. A (91 ± 2):(9 ± 1) **2**-d_2/**2**-d_1 mixture was converted to (*SR,RS*)-**4**-d_x as described in the synthesis of (*SR,RS*)-**4** above. The 70-eV mass spectrum of the product exhibited a *m/e* 597:598:599:600:601 ratio of 91.9:57.7:161.1:100.0:23.8. These data indicate a (*SR,RS*)-**4**-d_2/(*SR,RS*)-**4**-d_1 ratio of (31 ± 2):(69 ± 2).

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(50) Crocco, G. L. Ph.D. Thesis, University of Utah, 1986.