than that of the amino-amidine ligand also reflecting the different hybridization of the donor atoms.

Also in compound **3**, as already observed in **2**, the strict planarity of the aminic group at N(3) and the small value of the C(2)N(3)C(3)N(2) torsion angle [-26 (3)°] point to an extensive electron delocalization within the amidine group. Thus, according to the valence-bond theory, the amidine moiety can be described in terms of canonical forms A and B, Scheme II. In form B, which might also be stabilized by coordination to the metal, the N(2)-C(3) linkage has a single bond character which could account for the low energy of the cis-trans interconversion process. The phenyl group is slant [75 (1)°] against the amidine plane, probably because of steric interaction with the adjacent *tert*-butyl group, and does not contribute to the electron delocalization.

It is noteworthy that the free and coordinate ends of the amino-amidine ligand are linked together by a strong hydrogen bond [N(1)···N(2) = 2.80 (3) Å, N(2)-H(2)-N(1) = 167°] in such a way to form a pseudo-seven-membered ring which can be compared with the seven-membered metallacycle of compound **2** with a proton taking the place of platinum.

This finding gives a clue to the different isomerization about the C(3)=N(2) double bond observed in **3** as compared with **2**. In fact the two different conformations allow the platinum in **2** and the H(2) proton in **3** to come near to the aminic nitrogen [N(1)] and act as a ligating atom to close the seven-membered ring. This also indicates that the ligand molecule has a rather strong tendency to give such a cyclic structure which appears to be preferred either in the solid state or in solution.

The plane of the benzonitrile is nearly perpendicular to that of coordination [dihedral angle of 92 (1)°] as expected on the basis of steric interactions with cis ligands.

Conclusions

The reaction of a bidentate amine with *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ has shown that this very common substrate reacts readily with nucleophiles and the attack of one end of the diamine to a coordinate benzonitrile precedes the coordination of the second end to platinum. The monocoordinated amino-amidine ligand, formed in the first step of the reaction, undergoes cis-trans isomerization about the azomethine double bond and exhibits a strong tendency to form a seven-membered cyclic system either through formation of a strong hydrogen bond between the terminal aminic nitrogen and the platinum-bonded iminic nitrogen of amidine or through coordination of both ends to platinum.

Starting with *trans*-$[PtCl_2(NCPh)_2]$ the formation of a chelating amino-amidine ligand leads to a cationic complex, still bearing a coordinate benzonitrile, which reacts readily with base to give a benzamidate species. The benzamidate anion forms a strong hydrogen bond with the cis aminic group and slants on the coordination plane.

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Registry No. 1, 99727-69-2; **2**·CH_3OH, 99727-71-6; **3**·$^1/_2C_6H_5CH_3$, 99727-73-8; **4**, 89503-95-7; *trans*-$[PtCl_2(NCPh)_2]$, 51921-56-3; *cis*-$[PtCl_2(NCPh)_2]$, 15617-19-3; *t*-Bu_2en, 4062-60-6; benzonitrile, 100-47-0.

Supplementary Material Available: Listings of observed and calculated structure factors, hydrogen coordinates (Tables SI and SII), and thermal parameters (Tables SIII and SIV) (31 pages). Ordering information is given on any current masthead page.

Deprotonation and Anionic Rearrangements of Organometallic Compounds. 5. Kinetic vs. Thermodynamic Deprotonation in Reactions of Cyclopentadienylrhenium Acyl and Alkyl Complexes with Strong Bases

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Abstract: Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)(COR) (**1a**, R = CH_3; **1b**, R = $CH_2C_6H_5$; **1c**, R = C_6H_5; **1d**, R = H) with $Li^+{}^-N(CH(CH_3)_2)_2$ (LDA; THF, -78 °C) and then CH_3I gives (η^5-C_5H_4COR)Re(NO)(PPh_3)(CH_3) (**2a-d**, 50-78%). Deuterium-labeling experiments indicate that **1** is initially deprotonated to (η^5-C_5H_4Li)Re(NO)(PPh_3)(COR) (**3**), and ^{31}P NMR shows a subsequent rapid rearrangement (**3a**: <3 min, -95 °C) to Li^+ [(η^5-C_5H_4COR)Re(NO)(PPh_3)]$^-$ (**4**). Crossover experiments show **3** → **4** to be intramolecular. Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) with *n*-BuLi/TMEDA (-78 °C, 5 min) gives (η^5-C_5H_4Li)Re(NO)(PPh_3)($CH_2C_6H_5$) (**6**), which does not rearrange upon warming and yields (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)($CH_2C_6H_5$) (**7**, 74%) upon addition of CH_3I. When (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) ((+)-(*S*)-**8**, >98% ee) is treated with *n*-BuLi/TMEDA and then $(RCO)_2O$ (R = CH_3, $C_6H_5CH_2$, C_6H_5), (-)-(*S*)-**2a**, (-)-(*S*)-**2b**, and (-)-(*S*)-**2c**, all ≥98% ee, are obtained. Experiments with optically active **1** then show that **3a** → **4a** proceeds with >90% retention of configuration at rhenium and that **3b** → **4b** and **3c** → **4c** proceed with lesser degrees of retention and inversion, respectively. Pentamethylcyclopentadienyl complexes (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2R$) (**10a**, R = H; **10b**, R = C_6H_5) and *n*-BuLi react to give enolates Li^+(η^5-C_5Me_5)Re(NO)(PPh_3)(C(O^-)=CHR), which yield (η^5-C_5Me_5)Re(NO)(PPh_3)(COCH(R)CH_3) (72-82%) when treated with CH_3I. When **1b** is treated with the weaker base $Li^+{}^-N(Si(CH_3)_3)_2$, *E*-enolate Li^+(η^5-C_5H_5)-Re(NO)(PPh_3)(C(O^-)=CHC_6H_5 (**17**) forms and gives (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(C_6H_5)CH_3) ((*SR,RS*)-**16**) with 96% diastereoselectivity when treated with CH_3I. The factors controlling the stereoselectivity and site of deprotonation in these reactions, and the relationship of **3** → **4** to anionic organic rearrangements, are discussed.

Carbanions generated by the deprotonation of ligands of organometallic complexes are seeing increased applications in organic and organometallic synthesis.[1-3] For example, over the last few years a number of research groups have reported the generation

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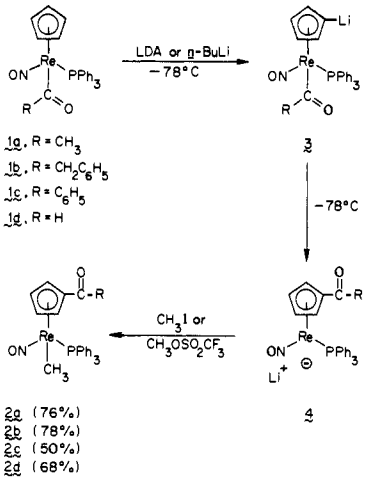
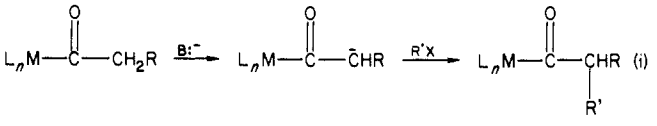
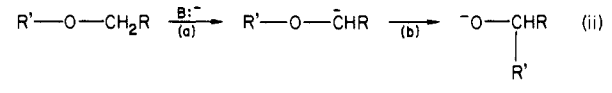
Scheme I. Deprotonation and Rearrangement of Acyl Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ (**1**)



of enolate anions derived from transition-metal acyl complexes, as shown in eq i.[2] These anions undergo ready alkylation, and when the metal moiety is chiral, impressive 1,3-asymmetric induction is often observed.[2a,c,e,j,k,m,n,p]



There is a rich migration chemistry that occurs when alkyl ligands attached to main group elements are deprotonated. For example, in the Wittig rearrangement (eq ii),[4] proton abstraction on a carbon adjacent to an ether oxygen (step a) is followed by facile alkyl migration to give an alkoxide anion (step b). Similar rearrangements occur when ammonium and sulfonium salts are deprotonated (Stevens rearrangement)[5] and in silicon-containing substrates (Brook rearrangement).[6] Surprisingly, few if any transition-metal analogues of such rearrangements are known.[7,8]



In this paper, we describe reactions of cyclopentadienylrhenium acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ (**1**)[9] with strong bases. Depending upon the substrate and conditions, either enolate formation (eq i) or rearrangement chemistry (eq ii) can occur. We also report related chemistry of alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ and pentamethylcyclopentadienyl acyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COR)$. From this study, a detailed picture of the acid/base properties of these molecules emerges.[10]

Results

I. Deprotonations of Cyclopentadienyl Ligands; Acyl Complexes. Acetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$ (**1a**)[9] was treated with LDA[11] (1.6–2.1 equiv) in THF at −78 °C (5–20 min). Subsequent addition of CH_3I (2–3 equiv) gave methyl complex $(\eta^5\text{-}C_5H_4COCH_3)Re(NO)(PPh_3)(CH_3)$ (**2a**) in 70–80% yields after chromatographic workup (Scheme I). No trace of propionyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_3)$[9] or isobutyroyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)_2)$[12]—plausible products if the acetyl ligand in **1a** had been deprotonated as in eq i—were detected. Complex **2a** was characterized as summarized in Table I. Its ^1H and ^{13}C NMR spectra showed patterns characteristic of a monosubstituted cyclopentadienyl ligand, and the methyl ^1H NMR resonance exhibited phosphorus coupling (J_{HP} = 5.7 Hz) typical for a $Re(PPh_3)(CH_3)$,[13] as opposed to a $(\eta^5\text{-}C_5H_4CH_3)Re(PPh_3)$ (J_{HP} < 1 Hz; see below), ligand array. The migration of the acetyl moiety from rhenium to carbon was also evidenced by an increase in $\nu_{C=O}$ from 1545 to 1664 cm^{-1}.

The generality of this transformation was probed with additional substrates, as summarized in Scheme I. Phenylacetyl complex **1b**, benzoyl complex **1c**, and formyl complex **1d** all underwent identical reactions with LDA and CH_3I (**1b**, **1c**) or $CH_3OSO_2CF_3$ (**1d**) to give methyl complexes $(\eta^5\text{-}C_5H_4COR)Re(NO)(PPh_3)(CH_3)$ (**2b–d**) in good yields. When **1b** was treated with LDA (−78 °C) and then Br_2 (2.1 equiv, −78 °C), bromide complex $(\eta^5\text{-}C_5H_4COCH_2C_6H_5)Re(NO)(PPh_3)(Br)$ (**5**) was obtained in 58% yield after workup. However, when **1a** or **1b** were treated with LDA and then acylating agents (benzoyl chloride, acetyl chloride, trifluoroacetic acid anhydride, phenylacetyl halides), a multitude of products formed.

One possible mechanism for the transformation **1** → **2** would entail initial cyclopentadienyl ligand deprotonation to give $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(COR)$ (**3**), followed by acyl ligand migration to give rhenium "anion" $Li^+[(\eta^5\text{-}C_5H_4COR)Re(NO)(PPh_3)]^-$ (**4**), as shown in Scheme I. It should be emphasized that the structural representation of **4** in Scheme I is approximate, as most metal anions ion pair to Li^+ (and Na^+) in THF,[14] and there are at least three possible binding sites in **4** (Re, NO oxygen, acyl oxygen). We sought evidence bearing on the mechanism in Scheme I.

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(10) A portion of this work has been communicated: (a) Heah, P. C.; Gladysz, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 7636. (b) Heah, P. C.; Gladysz, J. A. *J. Mol. Catal.* **1985**, *31*, 207.

(11) Abbreviations: (a) LDA = $Li^+{}^-N(CH(CH_3)_2)_2$. (b) TMEDA = *N,N,N',N'*-tetramethylethylenediamine. (c) Eu(Opt) = tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium. (d) DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

(12) Smith, D. E.; Gladysz, J. A. *Organometallics* **1985**, *4*, 1480.

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

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Labeled acetyl complex (η^5-C_5D_5)Re(NO)(PPh_3)($COCH_3$) (**1a**-d_5) was synthesized analogously to **1a**,[9] except that precursor complex (η^5-C_5D_5)Re(CO)$_3$ was prepared from $(CO)_5ReBr$ and readily available[15] TlC_5D_5. Mass spectrometric analysis indicated that a (90 ± 2):(10 ± 2) **1a**-d_5/**1a**-d_4 mixture was obtained. This sample was treated with LDA and then CH_3I as described above for **1a**. Subsequently isolated was methyl complex (η^5-$C_5D_4COCH_3$)Re(NO)(PPh_3)(CH_3) (**2a**-d_4; >98:2 d_4/d_3). This indicates that LDA abstracts a cyclopentadienyl proton of **1a** to give (η^5-C_5H_4Li)Re(NO)(PPh_3)($COCH_3$) (**3a**). Also, since the product **2a**-d_4 was of greater isotopic purity than the starting material **1a**-d_5, deprotonation must involve a substantial k_H/k_D.

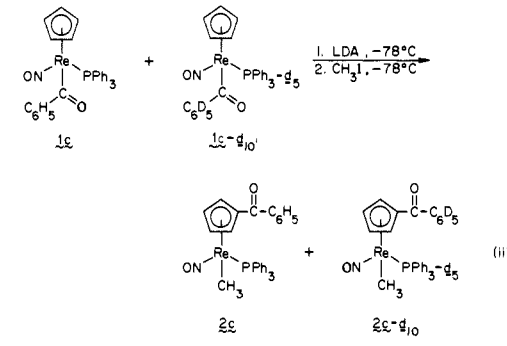
Others labeled complexes were also studied. Formyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CDO) (**1d**-d_1; (95 ± 2):(5 ± 2) d_1/d_0) gave, when treated with LDA and then $CH_3OSO_2CF_3$ as above, methyl complex (η^5-C_5H_4CDO)Re(NO)(PPh_3)(CH_3) (**2d**-d_1; (95 ± 2):(5 ± 2) d_1/d_0). A similar reaction of (η^5-C_5D_5)Re(NO)(PPh_3)(CDO) (**1d**-d_6; ca. 90:10 C_5D_5/C_5D_4H; ca. 95:5 CDO/CHO; total (82 ± 2):(16 ± 2):(2 ± 1) $d_6/d_5/d_4$) gave (η^5-C_5D_4CDO)Re(NO)(PPh_3)(CH_3) (**2d**-d_5; (88 ± 2):(12 ± 2) d_5/d_4). Reaction of acetyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($COCD_3$) (**1a**-d_3: >98:2 d_3/d_2) with LDA and then CH_3I gave (η^5-$C_5H_4COCD_xH_{3-x}$)Re(NO)(PPh_3)(CH_3) (**2a**-d_x) with x = 3, 2, 1, and 0. The remaining deuterium could be washed out of this **2a**-d_x by resubjecting it to the reaction conditions (0.2 equiv of LDA in THF, then CH_3I).

Having established the site of deprotonation in Scheme I, we next attempted the spectroscopic detection of intermediates. The reaction of acetyl complex **1a** with LDA was monitored by ^{31}P NMR spectroscopy at −95 °C. The starting material resonance (15.6 ppm) was immediately replaced (<3 min) by a broad multiplet centered at 43.8 ppm. No change was observed when the solution was warmed to −5 °C. The same result was obtained when *n*-BuLi (1.2 equiv) was used in place of LDA. However, *t*-BuLi gave numerous products. In other studies, we have noted that ^{31}P NMR resonances in the 40–47-ppm range are characteristic of anionic rhenium complexes $Li^+[(\eta^5\text{-}C_5H_4X)Re(NO)(PPh_3)]^-$.[16]

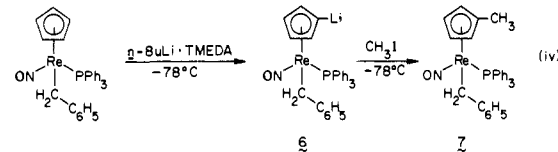
When CH_3I was added to the 43.8-ppm intermediate, methyl complex **2a** formed. When LDA was added to a 1:1 mixture of **1a** and CH_3I at −78 °C, **2a** was subsequently isolated as the major product (35%). We therefore conclude that $Li^+[(\eta^5\text{-}C_5H_4COCH_3)Re(NO)(PPh_3)]^-$ (**4a**) is the 43.8-ppm intermediate and that the acetyl migration **3a** → **4a** (Scheme I) is rapid at −95 °C.

The reaction of formyl complex **1d** with LDA was also monitored by ^{31}P NMR spectroscopy (−86 °C). The starting material resonance (16.0 ppm) was immediately replaced (<3 min) by a broad multiplet centered at 32.3 ppm. After 5 min, a new multiplet at 41.6 ppm was also observed. This species replaced the 32.3-ppm intermediate over the course of 50 min and showed no decomposition over the course of 1 h at room temperature. Subsequent addition of $CH_3OSO_2CF_3$ (2.6 equiv, −86 °C) gave **2d** (20.1 ppm) and other lesser products (25.3, 25.1, 24.7, 23.2 ppm) which, with time and/or warming, decreased as **2d** increased. Complexes of the type (η^5-C_5H_4Li)Re(NO)(PPh_3)(X) characteristically exhibit ^{31}P NMR resonances in the 25–35-ppm range (vide infra).[16] We tentatively suggest that (η^5-C_5H_4Li)Re(NO)(PPh_3)(CHO) (**3d**) is the 32.3-ppm intermediate,[16b] that Li^+ [(η^5-C_5H_4CHO)Re(NO)(PPh_3)]$^-$ (**4d**) is the 41.6-ppm intermediate, and that formyl migration (**3d** → **4d**) is slower than acetyl migration.

In order to establish the molecularity of the rearrangement **3** → **4**, several types of crossover experiments were conducted. First, co-reaction of a 1:1 mixture of benzoyl complexes **1c** and (η^5-C_5D_5)Re(NO)(PPh_3)(COC_6D_5) (**1c**-d_{10}) with LDA and CH_3I as above gave exclusively methyl complexes **2c** and (η^5-$C_5D_4COC_6D_5$)Re(NO)(PPh_3)(CH_3) (**2c**-d_9). No intermediate labels (**2c**-d_4, **2c**-d_5) were detected. Since this experiment could conceivably be biased against crossover due to an isotope effect in the deprotonation step, a 1:1 mixture of **1c** and (η^5-C_5H_5)-Re(NO)(PPh_3-d_5)(COC_6D_5) (**1c**-d_{10}') were co-reacted similarly (eq iii) and at two different concentrations (8.3 M, 31.3 M). In each case, only **2c** and (η^5-$C_5H_4COC_6D_5$)Re(NO)(PPh_3-d_5)(CH_3) (**2c**-d_{10}) were obtained. This experiment also excludes PPh_3 dissociation at any time during the reaction sequence. A 0.95:1.00 mixture of formyl complexes **1d** and (η^5-C_5D_5)Re(NO)(PPh_3)-(CDO) (**1**-d_6; (85 ± 2):(15 ± 2) d_6/d_5) was reacted with LDA and then $CH_3OSO_2CF_3$ as in Scheme I. The resulting **2d**-d_x consisted of a (92 ± 2):(8 ± 2) ratio of **2d**-d_0/**2d**-d_1 and a (85 ± 2):(15 ± 2) ratio of **2d**-d_5/**2d**-d_4. Hence, the rearrangement **3d** → **4d** is largely, but not necessarily entirely, intramolecular.



II. Deprotonation of Cyclopentadienyl Ligands; Alkyl Complexes. We sought to probe the generality of rhenium to η^5-C_5H_4Li ligand migration and determine the acyl migration stereochemistry. Hence, the deprotonation of alkyl complexes (η^5-C_5H_5)Re-(NO)(PPh_3)(R) was examined. Treatment of benzyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (eq iv; ^{31}P NMR, 24.4 ppm)[17] with 1.5 equiv of *n*-BuLi/TMEDA[11] in THF at −78 °C gave a rapid (<5 min) and quantitative conversion to (η^5-C_5H_4Li)Re(NO)(PPh_3)($CH_2C_6H_5$) (**6**), as assayed by ^{31}P NMR (25.8 ppm),[16b] and subsequent methylation (CH_3I, −78 °C) to (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)($CH_2C_6H_5$) (**7**, 74%). Treatment of (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) with *n*-BuLi also gave **6**, but complete reaction required 1.5 h at −24 °C. In a separate ^{31}P NMR monitored experiment, **6** showed no appreciable rearrangement or decomposition over the course of 30 min at 25 °C.



Treatment of methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**8**; ^{31}P NMR, 25.1 ppm)[13] with 2.1 equiv of *n*-BuLi/TMEDA in THF at −78 °C gave a slower (10 min) but still quantitative conversion to (η^5-C_5H_4Li)Re(NO)(PPh_3)(CH_3) (**9**), as assayed by ^{31}P NMR (28.2 ppm)[16b] and subsequent derivatization. Neither LDA nor *n*-BuLi effected deprotonation of **8** at −78 °C, and deprotonation was incomplete when only 1.5 equiv of *n*-BuLi/TMEDA was used. When **9** was treated with acetic anhydride (−24 °C), **2a** was obtained (38% conversion yield). When **9** was similarly treated with phenylacetic anhydride and benzoic anhydride, **2b** and **2c** were obtained. Reaction of **9** with either phenylacetyl chloride or bromide did not give **2b**. Complex **9**

(15) Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.

(16) (a) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 283. (b) We find[16a,c] the ^{31}P NMR resonances of (η^5-C_5H_4Li)Re-(NO)(PPh_3)(X) complexes to generally be sharp and 3–5 ppm downfield of precursor complexes (η^5-C_5H_5)Re(NO)(PPh_3)(X). However, the broad 32.3-ppm resonance we have provisionally assigned to **3d** (**1d**, 16.0 ppm) is an exception; this may be due to a structural perturbation such as binding of the formyl oxygen to the lithium of η^5-C_5H_4Li. (c) Crocco, G. L. Ph.D. Thesis, University of Utah, 1986.

(17) 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.

Table I. Spectroscopic Characterization of New Rhenium Complexes

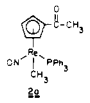
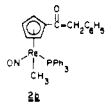
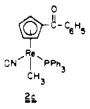
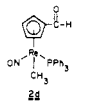
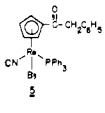
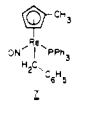
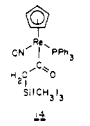
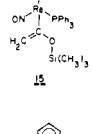
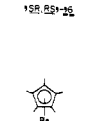
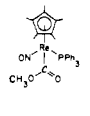
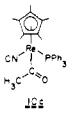
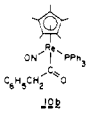
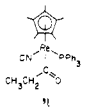
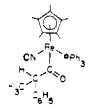
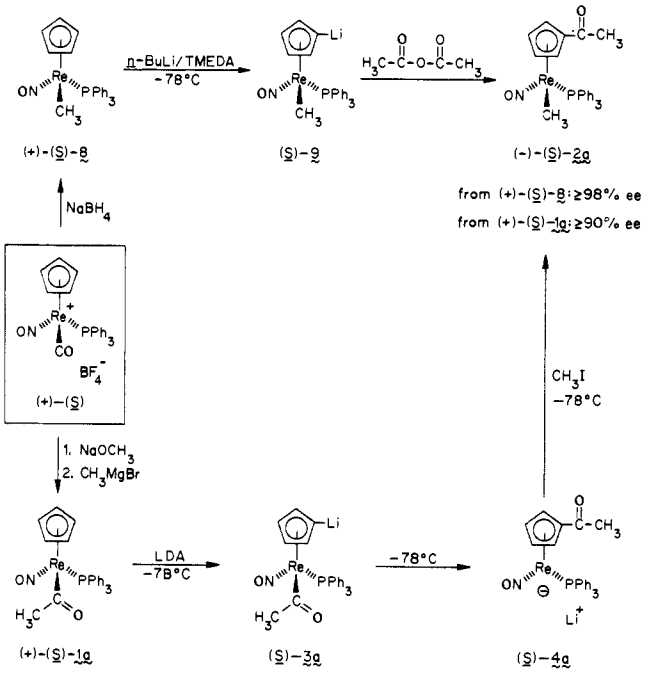
complex	IR (thin film, cm^{-1})	^1H NMR[a,b] (δ, $CDCl_3$)	^{13}C NMR[b,c] (ppm, CD_2Cl_2)	$^{31}P\{^1H\}$ NMR[d] (ppm, $CDCl_3$)	mass spectrum (m/e, 70 eV, ^{187}Re)
 2a	$\nu_{C=O}$ 1664 m $\nu_{N\equiv O}$ 1641 s	7.53–7.26 (m, 3 C_6H_5); 5.50, 5.24, 4.96, 4.14 (br m, C_5H_4); 2.22 (s, $COCH_3$); 0.82 (d, J = 5.7, $ReCH_3$)	194.2 (s, C=O); PC_6H_5 at 135.7 (d, J = 52.8, ipso), 134.2 (d, J = 10.9), 131.0 (s, p), 129.0 (d, J = 10.9); C_5H_4 at 101.8 (s), 95.9 (s), 95.8 (d, J = 5.6, ipso), 86.7 (s), 85.8 (s); 26.7 (s, $COCH_3$); –31.2 (d, J = 6.6, $ReCH_3$)	21.0	601 (M^+, 100%) 586 ($M^+ - CH_3$, 45%) 585 (28%) 543 ($M^+ - CH_3 - COCH_3$, 14%) 278 (Ph_3PO^+, 2%) 277 ($Ph_3PO^+ - H$, 6%) 262 (Ph_3P^+, 58%)
 2b	$\nu_{C=O}$ 1660 m $\nu_{N\equiv O}$ 1640 s	7.47–7.21 (m, 4 C_6H_5); 5.48, 5.27, 4.97, 4.12 (br m, C_5H_4); 3.78 (s, CH_2); 0.82 (d, J = 5.5, CH_3)	194.1 (s, C=O); CC_6H_5 at 135.9 (s, ipso), 130.2 (s), 129.0 (s), 127.3 (s); PC_6H_5 at 135.4 (d, J = 53.2, ipso), 134.2 (d, J = 10.5), 131.1 (s, p), 129.1 (d, J = 11.3); C_5H_4 at 103.0 (s), 96.1 (s), 95.0 (d, J = 5.7, ipso), 86.3 (s), 85.1 (s); 53.8 (s, CH_2); –30.4 (d, J = 6.9, CH_3)	21.0	677 (M^+, 57%) 662 ($M^+ - CH_3$, 14%) 661 (41%) 543 ($M^+ - CH_3 - COCH_2Ph$, 6%) 278 (Ph_3PO^+, 8%) 277 ($Ph_3PO^+ - H$, 20%) 262 (Ph_3P^+, 100%)
 2c	$\nu_{C=O}$ 1629 m $\nu_{N\equiv O}$ 1646 s	7.69–7.26 (m, 4 C_6H_5); 5.51, 5.28, 5.11, 4.32 (br m, C_5H_4); 0.92 (d, J = 5.5, CH_3)	192.5 (s, C=O); CC_6H_5 at 140.0 (s, ipso), 132.0 (s), 129.0 (s), 128.6 (s); PC_6H_5 at 135.6 (d, J = 53.2, ipso), 134.2 (d, J = 10.5), 131.0 (s, p), 129.1 (d, J = 10.2); C_5H_4 at 102.8 (s), 94.9 (s), 94.1 (d, J = 5.7, ipso), 88.2 (s), 87.8 (s); –30.0 (d, J = 6.9, CH_3)	20.6	663 (M^+, 55%) 648 ($M^+ - CH_3$, 14%) 647 (28%) 541 ($M^+ - CH_3 - COPh$, 6%) 278 (Ph_3PO^+, 4%) 277 ($Ph_3PO^+ - H$, 11%) 262 (Ph_3P^+, 100%)
 2d	$\nu_{C=O}$ 1673 m $\nu_{N\equiv O}$ 1638 s	9.27 (s, CHO); 7.47–7.33 (m, 3 C_6H_5); 5.57 (1 H), 5.01 (2 H), 4.56 (1 H) (br m, C_5H_4); 0.79 (d, J = 5.8, CH_3)[e]	185.5 (s, C=O); PC_6H_5 at 135.7 (d, J = 53.4, ipso), 134.3 (d, J = 10.6), 131.2 (s, p), 129.2 (d, J = 10.6); C_5H_4 at 100.7 (s), 95.7 (s, ipso), 92.4 (s), 90.4 (s), 87.6 (s); –30.5 (d, J = 7.0, CH_3)	19.7[e]	587 (M^+, 100%) 572 ($M^+ - CH_3$, 26%) 262 (Ph_3P^+, 72%)
 2e	$\nu_{C=O}$ 1665 m $\nu_{N\equiv O}$ 1685 s	7.83–6.83 (m, 4 C_6H_5); 5.47, 5.03, 4.83, 3.81 (br m, C_5H_4); 3.93 (s, CH_2)[f,g]	194.0 (s, C=O); CC_6H_5 at 135.4 (s, ipso), 130.5 (s), 129.0 (s), 127.3 (s); PC_6H_5 at 134.5 (d, J = 10.4), 134.4 (d, J = 54.2, ipso), 131.5 (s, p), 129.2 (d, J = 12.0); C_5H_4 at 109.6 (s), 101.0 (s), 96.7 (d, J = 8.2, ipso), 83.3 (s), 80.7 (s); 47.2 (s, CH_2)	12.9[g]	
 7	$\nu_{N\equiv O}$ 1628 s	8.03–7.37 (m, 4 C_6H_5); 5.84, 5.63, 5.18, 4.79 (br m, C_5H_4); 4.11 (dd, J_{HH} = 11.5, J_{PH} = 8.5, $ReCH_\alpha$); 3.26 (dd, J_{HH} = 11.5, J_{PH} = 2.0, $ReCH_\alpha'$); 2.36 (s, CH_3)[e]	CC_6H_5 at 159.9 (d, J = 3.5, ipso), 128.0 (s), 127.7 (s), 122.3 (s); PC_6H_5 at 137.0 (d, J = 50.8, ipso), 134.3 (d, J = 10.8), 130.6 (s, p), 129.0 (d, J = 10.8); C_5H_4 at 105.3 (s, ipso), 95.5 (d, J = 4.0), 92.3 (s), 89.6 (s), 86.3 (s); 13.4 (s, CH_3); –2.0 (d, J = 4.2, CH_2)	25.6[e]	649 (M^+, 21%) 558 ($M^+ - CH_2Ph$, 100%) 449 ($RePPh_3^+$, 8%) 387 ($M^+ - PPh_3$, 35%) 262 (PPh_3^+, 52%)
 14	$\nu_{N\equiv O}$ 1652 s $\nu_{C=O}$ 1535 m	7.51–7.36 (m, 3 C_6H_5); 5.20 (s, C_5H_5); 2.81 (d, J_{HH} = 10.6, CH_β); 1.48 (d, J_{HH} = 10.6, CH_β'); 0.06 (s, $Si(CH_3)_3$)	255.7 (d, J = 9.2, C=O); PC_6H_5 at 136.1 (d, J = 55.0, ipso), 134.3 (d, J = 10.7), 130.9 (s, p), 128.9 (d, J = 10.7); 93.7 (s, C_5H_5); 57.2 (s, CH_2); –0.51 (s, $Si(CH_3)_3$)[h]	16.6	
 15	$\nu_{N\equiv O}$ 1650 s	7.60–7.31 (m, 3 C_6H_5); 5.09 (s, C_5H_5); 4.52 (d, J = 1.8, CH_β); 3.99 (d, J = 1.0, CH_β'); 0.00 (s, $Si(CH_3)_3$)[e]	165.7 (d, J = 11.7, ReC); PC_6H_5 at 136.9 (d, J = 53.6, ipso), 134.6 (d, J = 11.1), 130.6 (d, J = 2.2, p), 128.6 (d, J = 10.3); 93.4 (s, CH_2); 91.9 (s, C_5H_5); 0.4 (s, $Si(CH_3)_3$)	21.5[e]	659 (M^+, 5%) 569 ($M^+ - C_3H_{10}OSi$, 10%) 544 ($M^+ - C_5H_{11}OSi$, 24%) 467 ($M^+ - C_5H_{11}OSi - Ph$, 10%) 435 (11%) 262 (Ph_3P^+, 100%)
 1SR,2SR-16	$\nu_{N\equiv O}$ 1650 s $\nu_{C=O}$ 1564 m	7.42–7.35 (m, 3 PC_6H_5); 7.04–6.48 (m, CC_6H_5); 5.18 (s, C_5H_5); 4.08 (q, J_{HH} = 7.4, CH); 1.49 (d, J_{HH} = 7.4, CH_3)	253.9 (d, J = 8.6, C=O); CC_6H_5 at 143.7 (s), 128.6 (s), 127.3 (s), 125.3 (s); PC_6H_5 at 136.4 (d, J = 54.9, ipso), 133.8 (d, J = 11.1), 130.5 (d, J = 2.2, p), 128.6 (d, J = 10.9); 92.7 (s, C_5H_5); 70.1 (s, CH); 19.8 (s, CH_3)[h]	15.7	678 (MH^+, 9%) 572 ($M^+ - C_8H_{10}$, 71%) 544 ($M^+ - C_9H_{10}O$, 10%) 263 (Ph_3PH^+, 40%) 262 (Ph_3P^+, 60%) 185 (Ph_2P^+, 100%)[i]
	$\nu_{N\equiv O}$ 1652 s $\nu_{C=O}$ 1583 m	7.35–6.96 (m, 3 C_6H_5); 3.37 (s, CO_2CH_3); 1.70 (s, 5 CH_3)[g]	202.0 (d, J = 12.7, C=O); PC_6H_5 at 135.9 (d, J = 51.8, ipso), 134.5 (d, J = 10.4), 130.0 (s, p), 128.2 (d, J = 10.4); 101.4 (s, $C_5(CH_3)_5$); 48.9 (s, CO_2CH_3); 9.6 (s, $C_5CH_3)_5$)[g]	21.3[g]	

Table I (Continued)

complex	IR (thin film, cm^{-1})	^1H NMR[a,b] (δ, $CDCl_3$)	^{13}C NMR[b,c] (ppm, CD_2Cl_2)	$^{31}P\{^1H\}$ NMR[d] (ppm, $CDCl_3$)	mass spectrum (m/e, 70 eV, ^{187}Re)
	$\nu_{N\equiv O}$ 1637 s $\nu_{C=O}$ 1552 m	7.60–7.20 (m, 3 C_6H_5); 1.88 (s, CH_3); 1.73 (s, 5 CH_3)	264.5 (d, J = 7.0, C=O); PC_6H_5 at 135.3 (d, J = 53.4, ipso), 134.3 (d, J = 11.2), 130.6 (s, p), 128.7 (d, J = 10.0); 102.6 (s, $C_5(CH_3)_5$); 50.8 (s, $COCH_3$); 9.8 (s, $C_5CH_3)_5$)[h]	19.0	657 (M^+, 11%) 642 ($M^+ - CH_3$, 100%) 614 ($M^+ - COCH_3$, 54%) 505 (8%) 262 (Ph_3P^+, 35%) 185 (Ph_2P^+, 26%)
	$\nu_{N\equiv O}$ 1636 s $\nu_{C=O}$ 1574 m	7.53–7.40 (m, 3 PC_6H_5); 7.21–7.08 (m, CC_6H_5); 3.66 (d, J_{HH} = 11.3, CH_β); 2.83 (d, J_{HH} = 11.3, CH_β'); 1.53 (s, 5 CH_3)	261.2 (d, J = 10.3, C=O); C_6H_5 at 138.0 (s), 130.7 (s), 128.3 (s), 125.6 (s); PC_6H_5 at 134.5 (d, J = 10.7 Hz), 130.5 (s, p), 128.8 (d, J = 10.6 Hz);[j] 102.7 (s, $C_5(CH_3)_5$); 71.4 (s, CH_2); 9.5 (s, $C_5(CH_3)_5$)[h]	17.3[k]	734 (MH^+, 23%) 642 ($M^+ - CH_2Ph$, 100%) 614 ($M^+ - COCH_2Ph$, 5%) 262 (Ph_3P^+, 31%) 185 (Ph_2P^+, 61%)[i]
	$\nu_{N\equiv O}$ 1636 s $\nu_{C=O}$ 1546 m	7.50–7.30 (m, 3 C_6H_5); 2.24 (dt, J_{HH} = 7.5, J_{HH} = 15.5, CH_β); 2.01 (dt, J_{HH} = 7.5, J_{HH} = 15.5, CH_β'); 1.73 (s, $C_5(CH_3)_5$); 0.50 (t, J_{HH} = 7.5, CH_2CH_3)	264.9 (d, J = 8.3, C=O); PC_6H_5 at 135.6 (d, J = 50.7, ipso), 134.4 (d, J = 11.1), 130.5 (s, p), 128.6 (d, J = 11.0); 102.3 (s, $C_5(CH_3)_5$); 56.9 (s, CH_2); 9.8 (s, $C_5(CH_3)_5$); 9.4 (s, CH_2CH_3)[h]	18.7	671 (M^+, 2%) 642 ($M^+ - C_2H_5$, 100%) 614 ($M^+ - COC_2H_5$, 41%) 505 (8%) 262 (Ph_3P^+, 14%) 185 (Ph_2P^+, 14%)
	$\nu_{N\equiv O}$ 1632 s $\nu_{C=O}$ 1548 m	7.46–7.39 (m, 3 PC_6H_5); 7.26–7.12 (m, CC_6H_5); 4.07 (q, J_{HH} = 6.8, CH); 1.38 (s, $C_5(CH_3)_5$); 0.36 (d, J_{HH} = 6.8, CH_3)	263.6 (d, J = 9.4, C=O); CC_6H_5 at 142.8 (s), 129.1 (s), 127.9 (s), 125.4 (s); PC_6H_5 at 133.9 (br s), 130.3 (s), 128.6 (d, J = 10.4);[j] 102.4 (s, $C_5(CH_3)_5$); 73.4 (s, CH); 15.6 (s, $CHCH_3$); 8.9 (s, $C_5(CH_3)_5$)[h]	18.0[k]	748 (MH^+, 10%) 642 ($M^+ - CH(CH_3)Ph$, 60%) 614 ($M^+ - COCH(CH_3)Ph$, 75%) 262 (Ph_3P^+, 42%) 185 (Ph_2P^+, 100%)[i]

[a] At 300 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$, unless noted; all couplings are in Hz. [b] All couplings (Hz) are to phosphorus unless noted. [c] At 75 MHz and ambient probe temperature and referenced to internal $(CH_3)_4Si$ unless noted. [d] At 32.2 MHz and ambient probe temperature and referenced to external 85% H_3PO_4, unless noted. [e] In CD_2Cl_2. [f] At 80 MHz. [g] In C_6D_6. [h] In $CDCl_3$ and referenced to $CDCl_3$ at 77.0 ppm. [i] Chemical ionization (CH_4) mass spectrum. [j] No ipso carbon observed. [k] In THF.

Scheme II. Reaction Cycle Establishing the Stereochemistry of the Acetyl Ligand Migration 3a → 4a



showed no appreciable rearrangement or decomposition over the course of 30 min at 25 °C.

With two distinct routes to **2a**, **2b**, and **2c** established, the stereochemistry of the rearrangement **3** → **4** could be probed. It was found that the chiral shift reagent Eu(Opt)[11] differentiated the CH_3 ^1H NMR resonances of racemic **2a**, **2b**, and **2c** in CD_2Cl_2. Hence, the optical purity of these complexes could be readily established.

First, methyl complex (+)-(*S*)-**8** (Scheme II),[18,19] >98% ee, was treated with *n*-BuLi/TMEDA and then acetic anhydride as was done with racemic **8** above. Levorotatory **2a** ($[\alpha]^{25}_{589}$ = −121°)[19c] was obtained, which was shown to be of ≥98% ee by Eu(Opt) assay. Similar reactions using phenylacetic anhydride and benzoic anhydride gave levorotatory **2b** ($[\alpha]^{25}_{589}$ = −430°)[19c] and levorotatory **2c** ($[\alpha]^{25}_{589}$ = −563°),[19c] both of ≥98% ee. Since these transformations occur without apparent rupture of any metal–ligand bonds, we assign the products as *S* enantiomers, corresponding to retention of configuration at rhenium, as shown for (−)-(*S*)-**2a** in Scheme II.

Next, the reaction of **1a** with LDA was repeated with (+)-(*S*)-**1a**, ≥98% ee. Addition of CH_3I after 6 min gave (−)-(*S*)-**2a** ($[\alpha]^{25}_{589}$ = −116°),[19c] which Eu(Opt) assay showed to be of ≥90% ee. This corresponds to *retention* of configuration at rhenium (Scheme II). In separate experiments, the CH_3I quench was postponed until 12 and 20 min after the addition of LDA. Subsequently isolated were (+)-(*S*)-**1a**, 20% ee, and racemic **1a**, respectively.

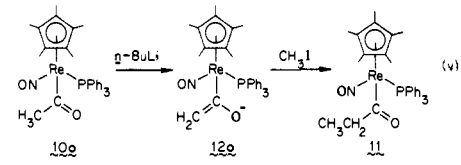
The reaction of **1b** with LDA and CH_3I was similarly repeated with (+)-(*S*)-**1b**, ≥98% ee. This gave (−)-(*S*)-**2b**, which Eu(Opt) assay showed to be of 32 ± 5% ee. An identical experiment was conducted with (−)-(*S*)-**1c**, 94% ee. This gave (+)-(*R*)-**2c**, 32 ± 5% ee. Thus, these transformations proceed with a moderate *overall* degree of retention and inversion, respectively. Depending

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

(19) (a) Absolute configurations are assigned according to the Baird/Sloan modification of the Cahn–Ingold–Prelog priority rules.[19d] The 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_4X > PPh_3 > NO > COR, CH_3. In complexes with more than one chiral center, the rhenium configuration is specified first. (b) Prefixes (+) and (−) refer to rotations at 589 nm. (c) All optical rotations are in CH_2Cl_2 with c in the range of 0.2 to 0.3 mg/mL. (d) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

upon the configurational stability of **4b** and **4c**, the rearrangement steps **3b** → **4b** and **3c** → **4c** may proceed with somewhat greater stereoselectivity.

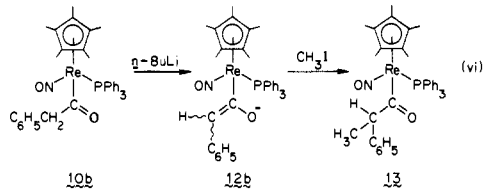
III. Routes to Deprotonated Acyl Ligands. Several independent syntheses of rhenium complexes containing deprotonated acyl ligands were attempted. First, pentamethylcyclopentadienyl acetyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_3$) (**10a**, eq v) was prepared from (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) and CH_3-MgBr analogously to **1a**.[9] New pentamethylcyclopentadienyl



10a 12a 11

complexes were characterized as summarized in Table I. Reaction of **10a** with *n*-BuLi (2.0 equiv) in THF was monitored by ^{31}P NMR spectroscopy at −70 °C. The starting material resonance (18.6 ppm) was rapidly replaced by a new resonance at 21.8 ppm. When CH_3I (2.5 equiv) was added, this peak slowly disappeared as a resonance at 18.7 ppm grew in. In a preparative-scale experiment, propionyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2CH_3$) (**11**) was isolated in 82% yield. Accordingly, the 21.8-ppm resonance was assigned to enolate Li^+(η^5-C_5Me_5)Re(NO)(PPh_3)($C(O^-)$=CH_2) (**12a**). In a separate ^{31}P NMR experiment, **12a** was found to be stable at −20 °C; at higher temperatures, decomposition occurred. An authentic sample of **11** was synthesized from (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) and CH_3CH_2MgBr (72%).

Having established that rhenium-substituted enolate anions can be generated, we next probed their potential for the stereoselective generation of new chiral centers. Phenylacetyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2C_6H_5$) (**10b**, eq vi) was prepared

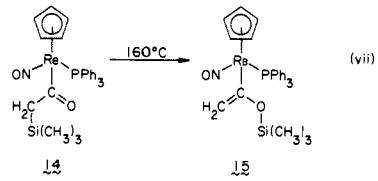


10b 12b 13

(96±1):(4±1) ratio of diastereomers

analogously to **10a**. Its reaction with *n*-BuLi (2.0 equiv) was monitored by ^{31}P NMR at −70 °C. The starting material resonance (17.3 ppm) was rapidly replaced by a new resonance at 25.8 ppm which was, by analogy to eq v, assigned to enolate Li^+(η^5-C_5Me_5)Re(NO)(PPh_3)($C(O^-)$=CHC_6H_5) (**12b**). When CH_3I (2.5 equiv) was then added, this resonance slowly disappeared as a new resonance at 21.8 ppm grew in. In a preparative-scale experiment, crystalline α-phenylpropionyl complex (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH(C_6H_5)CH_3$) (**13**) was isolated in 72% yield. This compound appeared pure by ^1H NMR, but HPLC analysis (silica gel; both before and after recrystallization) suggested that it was a (96 ± 1):(4 ± 1) ratio of diastereomers.

Since silyl enol ethers are often used as precursors to organic enolates,[20] we explored analogous routes to rhenium-substituted enolates. (Trimethylsilyl)acetyl complex (η^5-C_5H_5)Re(NO)-(PPh_3)($COCH_2Si(CH_3)_3$) (**14**, eq vii) was prepared from (η^5-

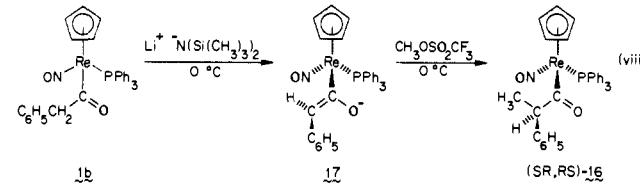


14 15

(20) (a) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: Boston, 1981; pp 217–221. (b) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598.

C_5H_5)Re(NO)(PPh_3)(CO_2CH_3) and $(CH_3)_3SiCH_2MgCl$ (61–68%). Thermolysis of **14** at 160 °C (eq v) gave silyl enol ether (η^5-C_5H_5)Re(NO)(PPh_3)($C(OSi(CH_3)_3)$=CH_2) (**15**; 59% spectroscopic yield) and acetyl complex **1a** in a 87:13 ratio. Complex **1a** presumably formed from adventitious protic impurities; repeated attempts to eliminate this byproduct or separate it from **15** failed. The mixture was treated with the anhydrous F^- source ($((CH_3)_2N)_3S^+Si(CH_3)_3F_2^-$ (25 °C, 12 h),[20b,21] but in all cases only the conversion of **15** to **1a** was observed. Complex **15** did not react with CH_3Li (THF) or CsF (CH_2Cl_2, THF) at room temperature.

Finally, we sought to determine if the mode of deprotonation in Scheme I might be altered by a weaker, more selective base.[22] Reaction of **1b** with Li^+ $^-N(Si(CH_3)_3)_2$ (3.2 equiv) was sluggish at 0 °C. After 16 h, $CH_3OSO_2CF_3$ was added (eq viii). Workup gave α-phenylpropionyl complex (η^5-C_5H_5)Re(NO)(PPh_3)-($COCH(C_6H_5)CH_3$) (**16**) in 53% yield. This compound appeared pure by ^1H NMR, but HPLC analysis (silica gel; both before and after recrystallization) indicated that it was a (98 ± 1):(2 ± 1) ratio of diastereomers. With use of methodology that has been communicated[12] and will be reported in detail elsewhere,[23] an authentic sample of (*SS*,*RR*)-**16**[19a] was prepared. The major product of eq viii was on this basis assigned as (*SR*,*RS*)-**16**



1b 17 (SR,RS)-16

In a separate experiment, eq viii was monitored by ^{31}P NMR. The generation of intermediate enolate Li^+(η^5-C_5H_5)Re(NO)-(PPh_3)($C(O^-)$=CHC_6H_5) (**17**, 20.1 ppm) was complete after 16 h at 0 °C or 4 h at 25 °C. A THF solution of **17** was kept at room temperature for 2 days. Only minor decomposition occurred, and no evidence (^{31}P NMR; $CH_3OSO_2CF_3$ quench) for the rearranged anion **4b** was found. When acetyl complex **1a** was treated with Li^+ $^-N(Si(CH_3)_3)_2$ as in eq viii, only slow decomposition occurred. No evidence for the generation of an enolate anion was noted by ^{31}P NMR.

Discussion

I. Site of Deprotonation. To rationalize the above chemistry, it is helpful to first review the known acid/base chemistry of η^5-C_5H_5 and acyl ligands. The deprotonation of η^5-C_5H_5 ligands by RLi reagents has abundant precedent.[24] For example, ferrocene is readily converted to the dilithio derivative (η^5-$C_5H_4Li)_2Fe$ and even more extensively lithiated species.[24] However, quantitative studies of the rates and equilibria of such reactions are scarce.

Setkina and co-workers used rates of H/D exchange in $C_2H_5O^-Na^+/C_2H_5OD$/benzene at 100 °C to estimate that the η^5-C_5H_5 protons of (η^5-C_5H_5)Fe$(CO)_2(C_6H_5)$ and (η^5-C_5H_5)Fe-$(CO)_2(CH_2C_6H_5)$ have pK_a's (ethanol/benzene) of 29 and 30, respectively.[25] In a recent study, we bounded the pK_a of the η^5-C_5H_5 protons of (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CN) as several units *greater* than the pK_a of CH_3CN in THF.[3] The pK_a of CH_3CN is 31.5 in H_2O and 31.3 in Me_2SO.[26] Since CH_2CN is not as electron withdrawing as COR,[27] the η^5-C_5H_5 protons

(21) Middleton, W. J. *Org. Syn.* **1985**, *64*, 221.
(22) (a) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232. (b) Fraser, R. R.; Mansour, T. S. *Ibid.* **1984**, *49*, 3443.
(23) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Georgiou, S.; Heah, P. C.; Hutchinson, J. P.; Rheingold, A. L.; Gladysz, J. A., manuscript in preparation.
(24) Walts, W. E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol 8, pp 1040–1044.
(25) (a) Orlova, T. Yu.; Setkina, V. N.; Sizoi, V. F.; Kursanov, D. N. *J. Organomet. Chem.* **1983**, *252*, 201. (b) Orlova, T. Yu.; Setkina, V. N.; Kursanov, D. N. *Ibid.* **1984**, *267*, 309.
(26) Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 4327.
(27) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; John Wiley & Sons: New York, 1975; Table 3-1.

should be more acidic in **1** than in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CN)$.

To our knowledge, the acidities of acyl ligand protons in L_nMCOCH_2R complexes have not been quantitatively studied. The pK_a's should, like those of the α-carbonyl protons in organic $XCOCH_2R$ compounds, depend upon the electronic properties of the L_nM moiety. On the basis of IR $\nu_{C=O}$ and chemical reactivity, most L_nM substituents appear to donate at least as much electron density into a carbonyl group as R_2N substituents.[9,28] Hence, metal acyl complexes should be among the more electron rich and therefore less acidic $XCOCH_2R$ compounds. The pK_a of $CH_3CON(CH_3)_2$ is, depending upon solvent, 31–34.[26] We believe this to be a reasonable estimate for the pK_a of the acetyl protons of **1a**. Hence, the $\eta^5\text{-}C_5H_5$ protons of **1a** are likely about as acidic as the acetyl protons. However, Bordwell has shown that α-phenyl substitution enhances amide acidity by ca. 7 pK_a units.[26] Therefore, the methylene protons of phenylacetyl complex **1b** should be considerably more acidic than the $\eta^5\text{-}C_5H_5$ protons.

In THF, the pK_a of $HN(Si(CH_3)_3)_2$ is 25.8 and the pK_a of $HN(CH(CH_3)_2)_2$ is 35.7.[22] Hence, the conjugate base of the latter, LDA, is more basic and less selective. Its reaction with phenylacetyl complex **1b**, which gives $\eta^5\text{-}C_5H_4Li$ complex **3b** (Scheme I), is clearly under kinetic control. Subsequent rapid acyl migration precludes attainment of equilibrium. The weaker, more selective, base $Li^+{}^-N(Si(CH_3)_3)_2$ discriminates, in a sluggish reaction (eq viii), for the more acidic phenylacetyl protons. That the resulting enolate **17** shows no tendency to rearrange to **3b** (or **4b**) is further evidence for the greater acidity of the phenylacetyl protons.

Why then do the $\eta^5\text{-}C_5H_5$ protons of **1a** and **1b** exhibit greater kinetic acidity than the acyl protons? There is an obvious statistical factor, and a possible steric factor. More importantly, however, it is well-known that for C–H bonds of comparable pK_a, deprotonation to give a resonance-stabilized carbanion is slow relative to deprotonation to give a localized carbanion.[29] The literature explanations for this effect[29] are easily applied to **1a** and **1b**. In the acyl ligand deprotonation **1b** → **17** (eq viii), rehybridization and charge delocalization to oxygen must occur. Hence, the full thermodynamic stability of the carbanion and the stabilizing influence of solvation[29d] will not be reflected until later in the reaction coordinate. The $\eta^5\text{-}C_5H_5$ ligand deprotonation **1b** → **3b** gives, however, a localized carbanion for which no rehybridization is required.[29b] Hence, the thermodynamic stability of the carbanion will be reflected earlier in the reaction coordinate, resulting in a lower transition-state energy.

A similar situation has been found with iron acetyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COCH_3)$. Reaction with LDA and then CH_3I gives a migration product derived from $\eta^5\text{-}C_5H_5$ ligand deprotonation, $(\eta^5\text{-}C_5H_4COCH_3)Fe(CO)_2(CH_3)$; reaction with $Li^+{}^-N(Si(CH_3)_3)_2$ and then CH_3I gives a product derived from acetyl ligand deprotonation, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COCH_2CH_3)$.[2d,o] However, with related complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$, bases LDA and *n*-BuLi give only acyl ligand deprotonation at −78 °C.[2b-e,30a]

When the $\eta^5\text{-}C_5H_5$ ligand in **1a** and **1b** is replaced by $\eta^5\text{-}C_5Me_5$, Scheme I chemistry is blocked and acyl ligand deprotonation is observed. However, the deprotonation of $\eta^5\text{-}C_5Me_5$ ligands is precedented.[30b,c] For example, when dication $[(\eta^5\text{-}C_5Me_5)Co(PMe_3)(CNR)]^{2+}$ is treated with $CD_3NO_2/(C_2H_5)_3N$, H/D exchange occurs.

II. Migration Chemistry. A number of ligand migrations to coordinated $\eta^5\text{-}C_5H_4Li$ have now been described.[7,16] The first, which was reported by Graham, was the conversion of $Ge(C_6H_5)_3$ complex $(\eta^5\text{-}C_5H_4Li)Mo(CO)_3(Ge(C_6H_5)_3)$ to $Li^+[(\eta^5\text{-}C_5H_4Ge(C_6H_5)_3)Mo(CO)_3]^-$.[7a] Berryhill has observed the rearrangement of $Si(CH_3)_3$ complex $(\eta^5\text{-}C_5H_4Li)Fe(CO)_2Si(CH_3)_3$ to $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_3)Fe(CO)_2]^-$.[7c,e] A similar reaction has been reported by Malisch.[7d] As noted above, acyl migrations of $(\eta^5\text{-}C_5H_4Li)Fe(CO)_2(COR)$ intermediates have been described.[2d,o] An interesting and likely related rearrangement occurs when cationic acyl complexes $[(\eta^5\text{-}C_5H_5)Co(PMe_3)_2(COAr)]^+$ are treated with DBU;[11] neutral *aryl*cyclopentadienyl complexes $(\eta^5\text{-}C_5H_4Ar)Co(PMe_3)(CO)$ are subsequently isolated.[7b] These migrations provide new and potentially useful approaches to functionally substituted cyclopentadienyl complexes.[31]

The conversion of formyl complex **1d** to **2d** constitutes the first stoichiometric carbon–carbon bond-forming reaction of a η^1-CHO ligand.[10b] Many metal-catalyzed CO/H_2 reactions involve intermediate formyl complexes, but further reduction is generally believed to be required before formation of a $>C_1$ species.[32] Recently, formyl complexes have been shown to be good hydrogen atom donors.[33] Thus, the small amount of apparent crossover product from the coreaction of **1d** and **1d**-d_6 with LDA might be radical initiated and not due to intermolecularity in the migration step **3d** → **4d**. The byproducts noted by ^{31}P NMR when **4d** is quenched with $CH_3OSO_2CF_3$ may be due to reversible methylation of the formyl moiety.

Migrations of ligands to coordinated $\eta^5\text{-}C_5H_5$ have also been observed, but these will not be detailed except to note that migration to $\eta^5\text{-}C_5H_4Li$ are considerably faster. For example, hydride migration to $\eta^5\text{-}C_5H_5$ in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ requires (as assayed by isotope scrambling) 80–120 °C,[34] whereas hydride migration to $\eta^5\text{-}C_5H_4Li$ in $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(H)$ occurs at −32 °C.[16a]

It is tempting to suggest that ligand migration to coordinated $\eta^5\text{-}C_5H_4Li$ might be a fairly general class of organometallic rearrangements. Contrast Scheme I with the key steps of the Wittig rearrangement shown in eq ii. In Scheme I an organometallic ligand on rhenium is deprotonated "adjacent" to the metal; in eq ii, an alkyl ligand on oxygen is deprotonated adjacent (α) to the oxygen. In Scheme I, an acyl ligand migrates to give a rhenium-centered anion; in eq ii, an alkyl ligand migrates to give an oxygen-centered anion. We do not wish to imply that the mechanisms of these transformations need be similar. Indeed, in contrast to **3** → **4**, Wittig-type rearrangements can be intermolecular.[4,35] However, both rearrangements have the related thermodynamic driving force of converting a carbanion to a heteroanion better able to accommodate the negative charge. Some conceptually related 1,2-ligand migrations involving transition metals have recently been analyzed by Hoffmann.[8]

The results in eq iv and Scheme II show that benzyl and methyl ligands do not migrate to $\eta^5\text{-}C_5H_4Li$. In single run experiments, we have also treated isopropyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)_2)$[36] and allyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CH_2)$[16a] with *n*-BuLi/TMEDA.[16c] In both cases, $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(R)$ species were cleanly gen-

(28) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

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

(30) (a) **Note Added in Proof**: In an important recent communication, S. G. Davies and co-workers report that at higher temperatures (−40 to 20 °C) *n*-BuLi can effect $\eta^5\text{-}C_5H_5$ ligand deprotonation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$ complexes. This is followed by an acyl ligand migration that is stereospecific at iron. They also find analogous rearrangements involving $-CO_2R$ ligands and $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(COCH_2R)$ complexes: Abbott, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgecock, I. M.; Maberly, T. R.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *289*, C13. (b) Werner, H.; Heisen, B.; Klingert, B.; Dölfel, R. *J. Organomet. Chem.* **1982**, *240*, 179. (c) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H. J.; Krüger, C. *Organometallics* **1983**, *2*, 1369.

(31) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1.

(32) (a) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (b) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (c) Dombek, D. B. *Adv. Catal.* **1983**, *32*, 325. (d) Henrici-Olivé, G.; Olivé, S. *J. Mol. Catal.* **1983**, *18*, 367.

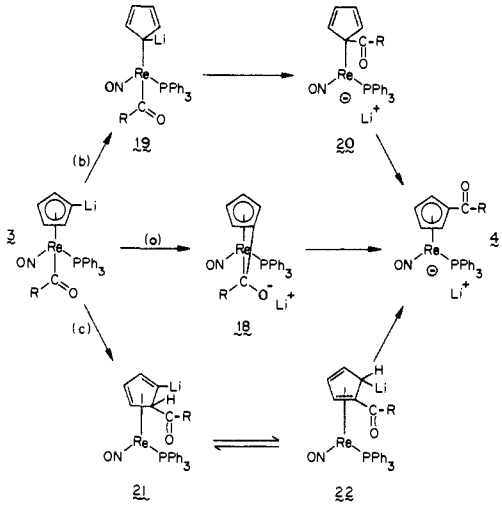
(33) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 5351. (b) Sumner, C. E.; Nelson, G. O. *Ibid.* **1984**, *106*, 132. (c) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (d) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

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

(35) Lansbury, P. T.; Pattison, V. A. *J. Org. Chem.* **1962**, *27*, 1933. Lansbury, P. T.; Patterson, V. A. *J. Am. Chem. Soc.* **1962**, *84*, 4295.

(36) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

Scheme III. Three Possible Mechanisms for the Acyl Migration 3 → 4



erated, as assayed by ^{31}P NMR. However, no rearrangement occurred upon warming to room temperature.

In Scheme II, we establish that the transformation **1a** → **2a** proceeds with ≥90% retention of configuration at rhenium. We then make the logical assumptions that the deprotonation step **1a** → **3a** and the methylation step **4a** → **2a** proceed with retention. From this, we conclude that the migration step **3a** → **4a** proceeds with ≥90% retention. However, it is in one sense surprising that any stereoselectivity is observed at all. In general, d^8 complexes of the type $(\eta^5\text{-}C_5H_5)ML_2$ are planar.[37] Although the location of the lithium in **4a** is uncertain, **4a** is likely (if it does not already exist as such) in facile equilibrium with a planar d^8 species. Accordingly, our CH_3I trapping data indicate that **4a** is of very limited configurational stability at −78 °C. The rearrangements **3b** → **4b** and **3c** → **4c** appear less stereoselective based upon CH_3I trapping; however, this may be due to the configurational instability of **4b** and **4c**.

It is surprising that **3c** → **4c** proceeds with a different stereochemistry (inversion) than **3a** → **4a** and **3b** → **4b**. This result has been reproduced several times and is based upon a stereochemical cycle analogous to the one in Scheme II. This result is also supported by an independent stereochemical cycle involving conversion of optically active **2c** to optically active benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$—both of which can be prepared from a common starting material, optically active $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$.[9] While we have no explanation for this differing behavior at present, it is not difficult to visualize. Retention corresponds to migration of the acyl ligand to the $\eta^5\text{-}C_5H_4Li$ coordination site, whereas inversion corresponds to $\eta^5\text{-}C_5H_4Li$ insertion into the acyl coordination site.

We have previously noted that the absolute configuration of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds correlates in nearly all cases with the sign of rotation at >500 nm.[9,18,38] Interestingly, this is strongly reversed for **2a–c**. These complexes also differ from **1a–d** and other $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes in being readily amenable to chiral NMR shift reagent ee assay.

III. Migration Mechanism. From the above data, it can be seen that the ligands which migrate to $\eta^5\text{-}C_5H_4Li$ most readily (GeR_3, SiR_3, COR) have low-lying acceptor orbitals. We delineate three possible classes of mechanisms of the migration step in Scheme III.

In the first mechanism a, the acyl ligand is directly transferred to the lithiated carbon. This could occur via intermediate **18** by an addition/elimination mechanism. However, a concerted migration is also conceivable.[39]

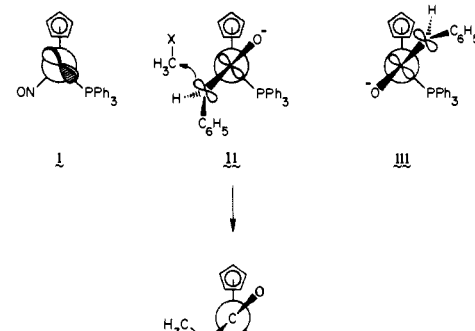
In the second mechanism b, initial $\eta^5\text{-}C_5H_4Li$ → $\eta^1\text{-}C_5H_4Li$ isomerization (**3** → **19**) occurs. We suggest that the Li substituent may facilitate this conversion, as the resulting ligand will have considerable aromatic cyclopentadienide character. Indeed, facile proton loss from $\eta^1\text{-}C_5H_5$ ligands, which would give a similar cyclopentadienide moiety, has been previously proposed in several reactions.[40]

In the third mechanism c, acyl migration occurs to a protonated $\eta^5\text{-}C_5H_4Li$ carbon (**3** → **21**). A 1,5 prototropic shift (or series thereof) would then give **22**, which could dissociate Li^+ to give **4**. Other examples of such ligand migrations/prototropic shifts are known.[34,41]

Variations of each of the above mechanisms can be easily generated. For example, the acyl oxygen might bond to the coordinatively unsaturated metal in **19–22**. Some steps (**3** → **19**, **3** → **21**) may be reversible.

Unfortunately, we are unable to rigorously distinguish among mechanisms a–c at this time. We believe that (a) is most likely to be stereospecific at rhenium, and Berryhill has proposed a similar mechanism for $Si(CH_3)_3$ migration to C_5H_4Li.[7e] However, the unusual[40] apparent migratory aptitude acetyl > formyl is difficult to rationalize. Mechanism c is unique in that the acyl group migrates to a carbon other than the one which is lithiated. However, our attempts to prepare a suitably labeled and reactive test substrate have not yet been successful.

IV. Generation of Enolate Anions and Stereochemistry of Alkylation. It is possible to deduce, with a few logical assumptions, the stereochemistry of enolate anion **17** (eq viii) from the stereochemistry of its methylation product (*SR,RS*)-**16**. First, note that **17** can be considered a vinyl complex. The C=C π bond is cross conjugated to a basic lone pair on rhenium and the oxygen lone pairs. The former is a d-type orbital—equivalent to the HOMO of the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)^+$ fragment—and is shown in I below.[17] The *E* geometric isomer of **17** is shown in II and III below in Re–C_α conformations in which the C=C bond is conjugated with this d orbital. We have previously shown for other vinyl rhenium complexes that the conformation corresponding to III, which is likely less stable on steric grounds, is far less reactive toward electrophiles.[12,23,42] Because of the oxygen cross conjugation, the reactive Re–C_α conformation is unlikely to correspond exactly to II; it would be easy to visualize, for example, the C=C bond of II in a more horizontal orientation.



Regardless of the exact Re–C_α orientation, the electrophile would be expected to attack the C=C bond opposite to the bulky PPh_3 ligand. Both C_β electrophilic attack upon analogous α-methoxyvinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHR)$[12,23] and C_α nucleophilic attack upon alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+PF_6^-$[17,36] have been shown

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to occur anti to PPh_3. It then follows that in order to obtain (*SR,RS*)-**16** (IV), **17** must be an *E* geometric isomer.

In elegant related work, S. G. Davies and L. Liebeskind have found that iron acyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$ can likewise be deprotonated to give *E*-enolates and that these undergo highly stereoselective alkylation.[2c,e,k,p] This system apparently does not suffer the disadvantage of competing $\eta^5\text{-}C_5H_5$ ligand deprotonation and involves a less expensive metal.

The stereochemical features of the (pentamethylcyclopentadienyl)rhenium enolate chemistry in eq vi are more difficult to discern. From trends in NMR spectra, it is tempting to conclude that the major diastereomer of **13** produced is (*SS,RR*)—opposite to the overall stereochemistry of eq viii. For example, in (*SR,RS*)-**16**, the methine hydrogen (δ 4.08) is upfield from the one in (*SS,RR*)-**16** (δ 4.29) and the methyl resonance is downfield (δ 1.49) from the one in (*SS,RR*)-**16** (δ 0.61). In the major diastereomer of **13**, the methine hydrogen (δ 4.07) is *downfield* from the one in the minor diastereomer (δ 3.82) and the methyl resonance (δ 0.36) is *upfield* from the one in the minor diastereomer (δ 1.40). Similar arguments have previously been used by Davies to assign relative configurations in iron acyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH(CH_3)R)$.[2i,k,p] If (*SS,RR*)-**13** is the major product of eq vi, then (if the same model used for eq vii is applicable) either the intermediate enolate is a *Z* isomer or electrophilic attack occurs opposite the $\eta^5\text{-}C_5Me_5$ ligand. Additional crystallographic and NMR studies will be needed to resolve these questions.

Carbon-to-oxygen 1,3-silatropic shifts are common in organic compounds.[43] The preparation of silyl enol ether **15** (eq vii) constitutes, to our knowledge, the first carbon-to-oxygen silatropic shift in a metal coordination sphere.[44] Although **15** did not prove to be a viable enolate precursor, we suggest that the silyl enol ether derived from **1b** could likely be converted to enolate **17**.

Conclusion

From this and related[1-3] studies, it is evident that organometallic compounds are providing a new frontier for carbanion chemistry. The deprotonation of C–H bonds in coordinated ligands is of mechanistic interest and gives carbanions that are synthetically useful and in some cases capable of novel rearrangement chemistry. It can be anticipated that research activity in this area will continue to dramatically increase.

Experimental Section

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

Solvents were purified as follows: THF and benzene, distilled from Na/benzophenone; hexanes and toluene, distilled from sodium; CH_2Cl_2, distilled from P_2O_5; $CHCl_3$ (spectrophotometric grade), degassed with N_2; CD_2Cl_2, distilled from CaH_2 or P_2O_5 and stored over activated 4A molecular sieves; CH_3OH, distilled from Mg.

Base LDA was prepared from *n*-BuLi and $HN(CH(CH_3)_2)_2$ in hexane[45] and standardized with 1,3-diphenyl-2-propanone tosylhydrazone.[46] Base *n*-BuLi was obtained from Aldrich and standardized[47] before use. The following were obtained from Aldrich or Alfa and used without standardization: CH_3MgBr, CH_3CH_2MgBr, $C_6H_5CH_2MgBr$, $(CH_3)_3SiCH_2MgCl$, $Li^+ {}^-N(Si(CH_3)_3)_2$. TMEDA was obtained from Aldrich and distilled from CaH_2.

Electrophiles were obtained and purified as follows: CH_3I (Aldrich), distilled from P_2O_5 and stored over Cu at 0 °C; $CH_3OSO_2CF_3$ (Aldrich), distilled from CaH_2; Br_2 (Aldrich), used without purification; $(CH_3CO)_2O$ (Aldrich), stored over quinoline and fractionally distilled; $(C_6H_5CO)_2O$ (Sigma), dissolved in benzene, washed with $NaHCO_3$, and recrystallized from benzene/petroleum ether; $(C_6H_5CH_2CO)_2O$, prepared by a literature procedure.[48] Eu(Opt) (Alfa) and CH_3ONa (MCB) were used as received.

Preparation of $(\eta^5\text{-}C_5H_4COCH_3)Re(NO)(PPh_3)(CH_3)$ (2a). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$ (**1a**, 70.8 mg, 0.121 mmol),[9] THF (6 mL) and a stir bar. The resulting yellow solution was cooled to −78 °C and LDA (600 μL, 0.43 M in hexanes, 0.258 mmol) was slowly added with stirring. The solution turned deep red, and after 20 min, CH_3I (20 μL, 0.321 mmol) was added. The solution turned orange and was stirred for 30 min at −78 °C. The solvent was then removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with CH_2Cl_2. The crude product was crystallized from layered acetone/hexanes at −24 °C. This gave red prisms of **2a** (55.3 mg, 0.092 mmol, 76%), mp 160–162.5 °C dec. Anal. Calcd for $C_{26}H_{25}O_2NPRe$: C, 52.00; H, 4.17. Found: C, 51.90; H, 4.37.

Preparation of $(\eta^5\text{-}C_5H_4COCH_2C_6H_5)Re(NO)(PPh_3)(CH_3)$ (2b). Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2C_6H_5)$ (**1b**, 61.4 mg, 0.093 mmol),[9] LDA (600 μL, 0.43 M in hexanes, 0.258 mmol), and CH_3I (20 μL, 0.321 mmol) were reacted as described in the preparation of **2a**. The solvent was then removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with 4:1 (v/v) hexanes/acetone. The crude product was crystallized from layered CH_2Cl_2/hexanes. This gave red prisms of **2b**·$(CH_2Cl_2)_{0.8\pm0.1}$ (49.3 mg, 0.073 mmol, 79%), mp 218.5–220 °C dec. Integration of a ^1H NMR spectrum confirmed a $(CH_2Cl_2)_{0.8\pm0.1}$ solvate. When crystals of **2b**·$(CH_2Cl_2)_{0.8\pm0.1}$ were dissolved in $CHCl_3$ and the solvent removed by rotary evaporation, unsolvated **2b** was obtained as an orange powder. Anal. Calcd for $C_{32}H_{29}O_2NPRe\cdot(CH_2Cl_2)_{0.75}$: C, 53.13; H, 4.12. Calcd for $C_{32}H_{29}O_2NPRe\cdot(CH_2Cl_2)_{0.8}$: C, 52.90; H, 4.11. Found: C, 53.23; H, 4.43.

Preparation of $(\eta^5\text{-}C_5H_4COC_6H_5)Re(NO)(PPh_3)(CH_3)$ (2c). Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COC_6H_5)$ (**1c**, 97.2 mg, 0.150 mmol),[9] LDA (880 μL, 0.43 M in hexanes, 0.378 mmol), and CH_3I (40 μL, 0.642 mmol) were reacted as described in the preparation of **2a**. The solvent was then removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with CH_2Cl_2. The crude product was crystallized from layered CH_2Cl_2/hexanes. This gave red prisms of **2c** (49.9 mg, 0.075 mmol, 50%), mp 190.5–193.0 °C dec. Anal. Calcd for $C_{31}H_{27}O_2NPRe$: C, 56.19; H, 4.08. Found: C, 56.40; H, 4.25.

Preparation of $(\eta^5\text{-}C_5H_4CHO)Re(NO)(PPh_3)(CH_3)$ (2d). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**1d**, 88.8 mg, 0.155 mmol),[13] THF (10 mL), and a stir bar. The resulting yellow solution was cooled to −78 °C and LDA (490 μL, 0.60 M in hexanes, 0.294 mmol) was slowly added with stirring. The solution turned deep red, and after 40 min, $CH_3OSO_2CF_3$ (45 μL, 0.398 mmol) was added. The solution turned orange and was stirred for 35 min at −78 °C. The solvent was removed under oil pump vacuum at room temperature. The major product was isolated by silica gel column chromatography with CH_2Cl_2. The crude product was diffusion crystallized from CH_2Cl_2/pentane. This gave red needles of **2d** (62.1 mg, 0.106 mmol, 68%), mp 133.5–135 °C dec. Anal. Calcd for $C_{25}H_{23}NO_2PRe$: C, 51.19; H, 3.92. Found: C, 51.19; H, 3.96.

Preparation of $(\eta^5\text{-}C_5H_4COCH_2C_6H_5)Re(NO)(PPh_3)(Br)$ (5). Complex **1b** (61.8 mg, 0.093 mmol), LDA (350 μL, 0.40 M in hexanes, 0.140 mmol), and Br_2 (10 μL, 0.195 mmol) were reacted as described in the preparation of **2b**. The major product was isolated by silica gel column chromatography with CH_2Cl_2. The crude product was crystallized from layered CH_2Cl_2/hexanes. This gave red plates of **5** (40.0 mg, 0.054 mmol, 58%), mp 210–211.5 °C dec. Anal. Calcd for $C_{31}H_{26}BrO_2NPRe$: C, 50.20; H, 3.51. Found: C, 50.13; H, 3.60.

Preparation of $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(CH_2C_6H_5)$ (7). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (62.1 mg, 0.098 mmol),[17] THF (8 mL), and a stir bar. The resulting orange solution was cooled to −24 °C and *n*-BuLi (350 μL, 0.56 M in hexane, 0.196 mmol) was added with stirring. The solution slowly turned a dark orange color, and after 1.5 h, CH_3I (12 μL, 0.196 mmol) was added. The reaction was stirred for an additional 20 min, and then solvent was removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with 1:1 (v/v) CH_2Cl_2/hexanes. The crude product was crystallized from layered CH_2Cl_2/hexanes. This gave orange plates of **7** (46.8 mg, 0.072 mmol, 74%), mp 180.5–184 °C. Anal. Calcd for $C_{31}H_{29}NOPRe$: C, 57.41; H, 4.47. Found: C, 57.44; H, 4.67.

(43) Reference 6, Table 4.
(44) For other silatropic shifts in organometallic compounds, see: Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.
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Preparation of 2a from (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (64.5 mg, 0.116 mmol),[13] THF (7 mL), and a stir bar. The resulting orange solution was cooled to −78 °C. Then TMEDA (20 μL, 0.133 mmol) followed by *n*-BuLi (125 μL, 2.4 M in hexane, 0.300 mmol) were added. The solution was stirred for 20 min and then $(CH_3CO)_2O$ (31 μL, 0.329 mmol) was added. The reaction was transferred to a −24 °C bath. After 25 min, solvent was removed under oil pump vacuum at room temperature. The products were isolated by silica gel column chromatography in CH_2Cl_2. This gave starting material (45 mg, 0.081 mmol, 70%) and **2a** (8 mg, 0.013 mmol, 38% based upon starting material consumed).

Preparation of (−)-(*S*)-2a from (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3). A Schlenk flask was charged with (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (5.5 mg, 0.010 mmol, >98% ee),[18] THF (4 mL), and a stir bar. The resulting orange solution was cooled to −78 °C. Then TMEDA (4 μL, 0.026 mmol) followed by *n*-BuLi (9 μL, 2.4 M in hexane, 0.021 mmol) were added. The solution was stirred for 10 min and then $(CH_3CO)_2O$ (2.5 μL, 0.027 mmol) was added. The reaction mixture was warmed to −24 °C. After 15 min, solvent was removed under oil pump vacuum at room temperature. The products were isolated by silica gel column chromatography in CH_2Cl_2. This gave starting material (1.0 mg) and (−)-(*S*)-**2a**; $[\alpha]^{25}_{589} = -121°$.[19c] Addition of Eu(Opt) established, as assayed by the $COCH_3$ ^1H NMR resonances, the optical purity of this material as ≥98% ee.

Preparation of (−)-(*S*)-2a from (+)-(*S*)-1a. A Schlenk flask was charged with (+)-(*S*)-**1a** (20.0 mg, 0.034 mmol, >98% ee),[9] THF (4 mL), and a stir bar. The resulting yellow solution was cooled to −78 °C and LDA (88 μL, 0.43 M in hexanes, 0.038 mmol) was added. After 6 min, CH_3I (3.5 μL, 0.056 mmol) was added. The orange solution was stirred for 5 min at −78 °C. The solvent was removed under oil pump vacuum at −24 °C, and (−)-(*S*)-**2a**, $[\alpha]^{25}_{589} = -116°$,[19c] was isolated by silica gel column chromatography in CH_2Cl_2. Optical purity (≥90% ee) was assayed with Eu(Opt) as described above.

Preparation of (−)-(*S*)-2b from (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3). A Schlenk flask was charged with (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (36.8 mg, 0.066 mmol), THF (6 mL), and a stir bar. The resulting orange solution was cooled to −78 °C. Then TMEDA (16 μL, 0.106 mmol) followed by *n*-BuLi (60 μL, 2.4 M in hexane, 0.144 mmol) were added. The solution was stirred for 1 h and then $(C_6H_5CH_2CO)_2O$ (58.6 mg, 0.231 mmol) was added. The reaction was warmed to −24 °C. After 20 min, solvent was removed under oil pump vacuum at room temperature. The products were isolated by silica gel column chromatography in CH_2Cl_2. This gave (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (26.6 mg, 0.048 mmol) and (−)-(*S*)-**2b** (6.2 mg, 0.009 mmol, 50% based upon starting material consumed), $[\alpha]^{25}_{589} = -430°$.[19c] Addition of Eu(Opt) established, as assayed by the $ReCH_3$ ^1H NMR resonances, the optical purity of this material to be >98% ee.

Preparation of (+)-(*S*)-1b. A Schlenk flask was charged with (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3) (101.3 mg, 0.168 mmol, >98% ee),[18] CH_2Cl_2 (5 mL), and a stir bar. The resulting yellow solution was cooled to −24 °C, and $C_6H_5CH_2MgCl$ (150 μL, 2.0 M in THF, 0.300 mmol) was added. The reaction was stirred for 15 min, and solvent was then removed under oil pump vacuum. The resulting yellow solid was extracted with acetone, and the extract was filtered through a plug of silica gel. The filtrate was concentrated to ca. 4 mL and 5 mL of hexanes was added. Yellow needles of (+)-(*S*)-**1b** formed over the course of 16 h at −24 °C and were collected by filtration and vacuum dried (49.0 mg, 0.074 mmol, 44%), mp 232–234 °C; $[\alpha]^{25}_{589} = 161.5°$.[19c]

Preparation of (−)-(*S*)-2b from (+)-(*S*)-1b. A Schlenk flask was charged with (+)-(*S*)-**1b** (21.0 mg, 0.032 mmol, >98% ee), THF (5 mL), and a stir bar. The resulting solution was cooled to −78 °C and LDA (80 μL, 0.43 M in hexanes, 0.344 mmol) was added. After 6 min, CH_3I (5.0 μL, 0.080 mmol) was added. The solution was stirred for 15 min at −78 °C. The solvent was removed under oil pump vacuum at −24 °C, and (−)-(*S*)-**2b** ($[\alpha]^{25}_{589} = 142°$,[19c] 15.0 mg, 0.022 mmol, 69%) was isolated by silica gel column chromatography in CH_2Cl_2. Addition of Eu(Opt) established, as assayed by the $ReCH_3$ ^1H NMR resonances, the optical purity of this material to be 32 ± 5% ee.

Preparation of (−)-(*S*)-2c from (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3). A Schlenk flask was charged with (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (20.4 mg, 0.037 mmol, >98% ee), THF (5 mL), and a stir bar. The resulting orange solution was cooled to −78 °C. Then TMEDA (7 μL, 0.046 mmol) followed by *n*-BuLi (28 μL, 2.4 M in hexane, 0.067 mmol) were added. The solution was stirred for 18 min and then $(C_6H_5CO)_2O$ (23.1 mg, 0.102 mmol) was added. The reaction mixture was warmed to −24 °C. After 10 min, solvent was removed under oil pump vacuum at room temperature. The products were isolated by silica gel column chromatography in CH_2Cl_2. This gave (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (9.8 mg, 0.018 mmol) and (−)-(*S*)-**2c** (7.6 mg, 0.011 mmol, 60% based upon starting material consumed), $[\alpha]^{25}_{589} = -563°$.[19c] Addition of Eu(Opt) established, as assayed by the $ReCH_3$ ^1H NMR resonances, the optical purity of this material to be >98% ee.

Preparation of (+)-(*R*)-2c from (−)-(*S*)-1c. A Schlenk flask was charged with (−)-(*S*)-**1c** (25.5 mg, 0.039 mmol, 94% ee),[18] THF (5 mL), and a stir bar. The resulting solution was cooled to −78 °C and LDA (135 μL, 0.43 in hexanes, 0.058 mmol) was added. After 6 min, CH_3I (4.8 μL, 0.078 mmol) was added. The orange solution was stirred for 5 min at −78 °C. The solvent was removed under oil pump vacuum at −24 °C, and (+)-(*R*)-**2c** ($[\alpha]^{25}_{589} = 186°$,[19c] 12.5 mg, 0.019 mmol, 48%) was isolated by silica gel column chromatography in CH_2Cl_2. Addition of Eu(Opt) established, as assayed by the $ReCH_3$ ^1H NMR resonances, the optical purity of this material to be 32 ± 5% ee.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3). A Schlenk flask was charged with $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (889.2 mg, 1.181 mmol),[49] anhydrous CH_3OH (50 mL), and a stir bar. Then $NaOCH_3$ (255.1 mg, 4.722 mmol) was added, and the reaction was stirred overnight. Then solvent was removed by rotary evaporation, and the dark yellow residue was extracted with CH_2Cl_2. The extract was passed through a plug of Celite. Solvent was removed from the filtrate by rotary evaporation, which gave a yellow bubble-up solid. The solid was washed with hexanes, which gave spectroscopically pure (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) as a yellow powder (744 mg, 1.107 mmol, 94%). This was used for subsequent reactions. An analytical sample was crystallized from layered CH_2Cl_2/hexanes. This gave yellow needles, mp 175–177 °C dec. Anal. Calcd for $C_{30}H_{33}NO_3PRe$: C, 53.57; H, 4.91. Found: C, 53.78; H, 5.20.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_3$) (10a). A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) (412.9 mg, 0.614 mmol), toluene (35 mL), and a stir bar. Then CH_3MgBr (0.8 mL, 3.0 M in ether, 2.4 mmol) was added and the reaction was stirred for 1 h. Solvent was then removed by rotary evaporation, and the resulting yellow residue was extracted with acetone. The extract was passed through a plug of silica gel and solvent was removed from the filtrate by rotary evaporation. The resulting yellow solid was crystallized from layered CH_2Cl_2/hexanes. This gave dark yellow needles of **10a** (354.2 mg, 0.540 mmol, 88%), mp 231–234 °C dec. Anal. Calcd for $C_{30}H_{33}NO_2PRe$: C, 54.88; H, 5.03. Found: C, 54.68; H, 5.19.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2CH_3$) (11). (A) A Schlenk flask was charged with **10a** (62.5 mg, 0.096 mmol), THF (7 mL), and a stir bar. The resulting yellow solution was cooled to −63 °C and *n*-BuLi (90 μL, 2.4 M in hexane, 0.216 mmol) was added. The solution turned red, and after 40 min, CH_3I (18 μL, 0.289 mmol) was added. The solution turned orange and was stirred for 20 min at −63 °C. The solvent was then removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with 50:50 (v/v) acetone/hexanes. Recrystallization from CH_2Cl_2/hexanes gave orange crystals of **11** (52.1 mg, 0.078 mmol, 82%), mp 240–241 °C dec. (B) Complex (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) (262.0 mg, 0.390 mmol) and CH_3CH_2MgBr (0.55 mL, 2.9 M in ether, 1.60 mmol) were reacted as in the preparation of **10a** above. An identical workup gave a yellow residue which was crystallized from layered CH_2Cl_2/hexanes. This gave orange needles of **11** (187.0 mg, 0.279 mmol, 72%), mp 242–243 °C dec. Anal. Calcd for $C_{31}H_{35}NO_2PRe$: C, 55.52; H, 5.22. Found: C, 55.58; H, 5.08.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH_2C_6H_5$) (10b). A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(CO_2CH_3) (415.6 mg, 0.619 mmol), toluene (25 mL), and a stir bar. The solution was stirred at room temperature and $C_6H_5CH_2MgCl$ (1.24 mL, 2.0 M in THF, 2.480 mmol) was added. After 45 min, solvent was removed by rotary evaporation. The solid was extracted with acetone, and the extract was filtered through a plug of silica gel. The filtrate was concentrated by rotary evaporation to ca. 8 mL. An equal volume of hexanes was added. Orange prisms of **10b** formed over the course of 16 h at −24 °C and were collected by filtration and vacuum dried (297.0 mg, 0.406 mmol, 66%), mp 200–204 °C dec. A second crop (12.0 mg, 0.016 mmol, 3%) was obtained from the mother liquor. Anal. Calcd for $C_{36}H_{37}NO_2PRe$: C, 59.02; H, 5.05. Found: C, 58.83; H, 4.85.

Preparation of (η^5-C_5Me_5)Re(NO)(PPh_3)($COCH(C_6H_5)CH_3$) (13). A Schlenk flask was charged with **10b** (52.2 mg, 0.071 mmol), THF (5 mL), and a stir bar. The resulting yellow solution was cooled to −78 °C and *n*-BuLi (65 μL, 2.4 M in hexane, 0.156 mmol) was added. The solution turned red, and after 45 min, CH_3I (16 μL, 0.256 mmol) was added. The reaction was stirred for 25 min at −78 °C. The solvent was then removed under oil pump vacuum at 0 °C. The major product was isolated by silica gel column chromatography with CH_2Cl_2. HPLC analysis indicated a (96 ± 1):(4 ± 1) ratio of diastereomers. Recrys-

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tallization from acetone/pentane gave orange prisms of **13** (38.2 mg, 0.051 mmol, 72%), mp 204–208 °C dec. Anal. Calcd for $C_{37}H_{39}NO_2PRe$: C, 59.52; H, 5.23. Found: C, 59.37; H, 5.53.

Preparation of (η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH$_2$Si(CH$_3$)$_3$) (14). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh$_3$)(CO$_2$CH$_3$) (300 mg, 0.498 mmol),[9] toluene (30 mL), and a stir bar. Then $(CH_3)_3SiCH_2MgCl$ (1.75 mL, 1.0 M in ether, 1.75 mmol) was added and the reaction was stirred for 10 h. Then 2 mL of freshly distilled CH_3OH was added and the solvents were removed under oil pump vacuum. The resulting yellow residue was extracted with benzene (3 × 10 mL; glovebox) and filtered through a coarse porosity frit. Solvent was removed from the filtrate under oil pump vacuum. The yellow residue was extracted with CH_2Cl_2. Then three volumes of hexanes were added. Solvent was removed under oil pump vacuum to give **14** as a yellow powder (212 mg, 0.322 mmol, 65%), mp 153–154 °C dec. An analytical sample was prepared by taking **14** (30 mg) up in ether (4 mL), adding heptane (8 mL), and concentrating by rotary evaporation. Anal. Calcd for $C_{28}H_{31}NO_2SiPRe$: C, 51.06; H, 4.71. Found: C, 51.23; H, 4.85.

Preparation of (η^5-C_5H_5)Re(NO)(PPh$_3$)(C(OSi(CH$_3$)$_3$)=CH$_2$) (15). A 200 × 6 mm glass tube was charged with **14** (90 mg, 0.137 mmol), evacuated for 30 min, and sealed. The tube was then immersed in a 160 °C oil bath for 20 min. The yellow solid melted with some gas evolution. The resulting dark red melt was allowed to cool to room temperature, and the reaction was transferred to a glovebox for the remaining workup. The melt was extracted with THF and the solvent removed by high vacuum rotary evaporation to give a yellowish-brown bubble up solid. This solid was then extracted with 2 × 2.5 mL of ether. The ether was removed by high vacuum rotary evaporation to give a yellow bubble-up solid (60 mg), which ^{1}H NMR analysis showed to be a 87:13 mixture of **15** (0.81 mmol, 59%) and **1a**. Attempts to remove the **1a** by extraction and recrystallization were unsuccessful.

Preparation of (*SR*,*RS*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(C$_6$H$_5$)CH$_3$) ((*SR*,*RS*)-16). A Schlenk flask was charged with **1b** (200 mg, 0.302 mmol), THF (4 mL), and a stir bar. The resulting yellow solution was cooled to 0 °C and $Li^+{}^-N(Si(CH_3)_3)_2$ (970 μL, 1.0 M in hexanes, 0.970 mmol) was added. Within 30 min, the solution turned deep red. The solution was kept at 0 °C overnight, and then $CH_3OSO_2CF_3$ (125 μL, 1.105 mmol) was added. The solution was then stirred for 30 min at room temperature. Solvent was removed under oil pump vacuum, and the residue was chromatographed on silica gel with CH_2Cl_2. Some starting material (18.1 mg, 0.027 mmol, 9%) was recovered, and (*SR*,*RS*)-**16** was obtained. This material was recrystallized from layered CH_2Cl_2/hexanes, which gave yellow needles (99 mg, 0.146 mmol, 53% based upon starting material consumed), mp 194–196 °C dec. HPLC analyses before and after recrystallization indicated a (98 ± 1):(2 ± 1) ratio of diastereomers. Anal. Calcd for $C_{32}H_{29}NO_2PRe$: C, 56.80; H, 4.29. Found: C, 56.57; H, 4.40.

Monitoring of Reactions by ^{31}P NMR. The following experiment is representative. A 5-mm NMR tube was charged with **1a** (15 mg, 0.026 mmol) and THF (0.35 mL) and capped with a septum. A ^{31}P NMR spectrum was recorded at −95 °C (15.6 ppm). The tube was then cooled to −98 °C in a CH_3OH/liquid nitrogen slush bath. Then LDA in hexanes (95 μL, 0.43 M, 0.041 mmol) was added. The sample was shaken and immediately transferred back to the −95 °C NMR probe. A broad singlet, 43.8 ppm, was observed.

Deuterated Compounds. Compounds not described below were prepared by obvious modifications of published routes to unlabeled compounds. **(η^5-C_5D_5)Re(CO)$_3$**:[50] A Schlenk flask was fitted with a reflux condenser and was charged with C_5D_5Tl (1.49 g, 5.438 mmol),[15] $(CO)_5ReBr$ (2.00 g, 4.926 mmol), benzene (40 mL), and a stir bar. The reaction was refluxed with stirring for 24 h. The resulting suspension of a white solid in a yellow solution was filtered, and the white residue obtained was extracted with 3 × 30 mL of CH_2Cl_2. The organic fractions were combined and solvents were removed by rotary evaporation. The resulting off-white residue was sublimed (80 °C, 0.05 mmHg) to give white crystals of (η^5-C_5D_5)Re(CO)$_3$ (1.457 g, 4.285 mmol, 87%). **(C$_6$H$_5$)$_2$P(C$_6$D$_5$)** was prepared from $(C_6H_5)_2PCl$ and C_6D_5MgBr according to a literature procedure.[51] **Analysis**: The isotopic purity of C_5D_2Tl was assayed by 70-eV mass spectral analysis. In a typical preparation,[15] the *m/e* 272:273:274:275 ratio was 3.8:43.1:8.8:100, while the *m/e* 268:270 ratio for natural abundance C_5H_5Tl under identical conditions was 47.3:100. From these data, the C_5D_5Tl:C_5D_5HTl ratio was calculated to be (90 ± 2):(10 ± 2). The isotopic purity of formyl complex **1d**-d_x was assayed by similar mass spectral analysis of its BH_3·THF reduction product,[13] (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$)-d_x. Other compounds were assayed directly.

Labeling Experiments. (A) A (90 ± 2):(10 ± 2) mixture of (η^5-C_5D_5)Re(NO)(PPh$_3$)(COCH$_3$) and (η^5-C_5D_4H)Re(NO)(PPh$_3$)(COCH$_3$) was converted to **2a** as described above. The 70-eV mass spectrum of the product exhibited a *m/e* 545:546:547:548 ratio of 63.9:27.0:100:25.9. Under identical conditions, the *m/e* 541:542:543:544 ratio for natural abundance **2a** was 64.4:29.5:100:24.7. These data indicate a **2a**-d_4/**2a**-d_3 ratio of >98:2. (B) A (95 ± 2):(5 ± 2) mixture of (η^5-C_5H_5)Re(NO)(PPh$_3$)(CDO) (**1a**-d_1) and **1a**-d_0 was converted to **2d** as described above. The 70-eV mass spectrum of the product exhibited a *m/e* 585:586:587:588:589:590 ratio of 3.3:60.8:21.2:100:27.9:4.1. Under identical conditions the *m/e* 585:586:587:588:589 ratio for natural abundance **2d** was 58.4:17.4:100:27.9:3.8. These data indicate a **2d**-d_1:**2d**-d_0 ratio of (95 ± 2):(5 ± 2). (C) A mixture of **1c** (18.0 mg, 0.028 mmol) and (η^5-C_5D_5)Re(NO)(PPh$_3$)(COC$_6$D$_5$) (**1c**-d_{10}; (90 ± 2):(10 ± 2) d_{10}/d_9; 18.6 mg, 0.028 mmol) in THF (6 mL) was converted to **2c** as described above. The 70-eV mass spectrum of the product was the superposition of the mass spectra of independently prepared **2c** and **2c**-d_9. (D) A mixture of **1c** (15.2 mg, 0.024 mmol) and (η^5-C_5H_5)Re(NO)(PPh$_3$-d_5)(COC$_6$D$_5$) (**1c**-d_{10}; (98 ± 1):(2 ± 1) d_{10}/d_9; 15.5 mg, 0.024 mmol) in THF (1.5 mL) was converted to **2c** as described above. The 70-eV mass spectrum of the product was the superposition of the mass spectra of independently prepared **2c** and **2c**-d_{10}. (E) A mixture of **1d** (19.0 mg, 0.033 mmol) and (η^5-C_5D_5)Re(NO)(PPh$_3$)(CDO) (**1d**-d_6; (82 ± 2):(16 ± 2):(2 ± 1) $d_6/d_5/d_4$; 20.0 mg, 0.035 mmol) in THF (6 mL) was converted to **2d** as described above. The 70-eV mass spectrum of the product showed a *m/e* 585:586:587:588:589:590:591:592:593 ratio of 61.0:25.0:100:35.6:18.1:72.9:34.6:128:33.8. From the *m/e* 585:586:587:588 ratio of natural abundance **2d** noted above, a (92 ± 2):(8 ± 2) ratio of **2d**-d_0/**2d**-d_1 was calculated. From the *m/e* 590:591:592:593 ratio of **2d** derived from an independently reacted sample of **1d**-d_6, a (85 ± 2):(15 ± 2) ratio of **2d**-d_5/**2d**-d_4 was calculated.

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Registry No. 1a, 82582-46-5; (+)-(*S*)-**1a**, 87480-06-0; **1b**, 82582-48-7; (+)-(*S*)-**1b**, 100017-75-2; **1c**, 76770-59-7; (−)-(*S*)-**1c**, 87480-05-5; **1d**, 70083-74-8; **2a**, 93304-78-0; (−)-(*S*)-**2a**, 93381-97-6; **2b**, 93304-82-6; (−)-(*S*)-**2b**, 100017-74-1; **2c**, 93304-80-4; (−)-(*S*)-**2c**, 100018-81-3; (+)-(*R*)-**2c**, 100017-76-3; **2d**, 98606-30-5; **5**, 93304-87-1; **7**, 93304-85-9; **10a**, 99901-55-0; **10b**, 99901-57-2; **11**, 99901-56-1; **13**, 99901-58-3; **14**, 99921-92-3; **15**, 99921-93-4; (*SR*,*RS*)-**16**, 99901-59-4; (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$), 71763-28-5; (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$), 71763-18-3; (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$), 82336-24-1; (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(CO$_2$CH$_3$), 87480-09-9; (η^5-C_5Me_5)Re(NO)(PPh$_3$)(CO$_2$CH$_3$), 99901-54-9; [(η^5-C_5Me_5)Re(NO)(PPh$_3$)(CO)]$^+$BF$_4^-$, 86497-31-6; (η^5-C_5D_5)Re(CO)$_3$, 99901-60-7; C_5D_5Tl, 64055-35-2; $(CO)_5ReBr$, 14220-21-4.

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