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Synthesis and Chemistry of Chiral Rhenium Acyls (η-C_5H_5)Re(NO)(PPh_3)(COR)

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Rhenium acyls (η-C_5H_5)Re(NO)(PPh_3)(COR) (R = CH_3 (**2**), CH_2CH_3 (**3**), CH_2-*n*-C_8H_{17} (**4**), C_6H_5 (**5**), $CH_2C_6H_5$ (**6**), $CH_2CH_2C_6H_5$ (**7**), $CH{=}CH_2$ (**8**), $CH_2CH{=}CH_2$ (**9**)) are prepared in high yield by RMgX attack upon (η-C_5H_5)Re(NO)(PPh_3)($COOCH_3$) (**1**). Acyl (η-C_5H_5)Re(NO)(PPh_3)($COC{\equiv}CCH_3$) (**10**) is prepared by $LiC{\equiv}CCH_3$ attack upon [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$. Acyls **2**, **5**, and **7** are also prepared in optically active form from optically active **1**. These compounds are characterized by IR, ^1H NMR, ^{13}C NMR, and (when optically active) ORD and CD. They are shown to undergo high-yield (1) BH_3 reduction ((−)-(*R*)-**2**, **4**, (+)-(*R*)-**5**, **7**) to the corresponding alkyls (η-C_5H_5)Re(NO)(PPh_3)(CH_2R), (2) methylation with CH_3SO_3F/NH_4^+ PF_6^- (**2**, **5**) to methoxycarbenes [(η-C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)R)]$^+$ PF_6^-, and (3) protonation with CF_3SO_3H (**2**, **3**) to hydroxycarbenes [(η-C_5H_5)Re(NO)(PPh_3)(=C(OH)R)]$^+CF_3SO_3^-$. Structures for the preferred conformers of **2**–**10** and their methylation and protonation products are suggested.

Introduction

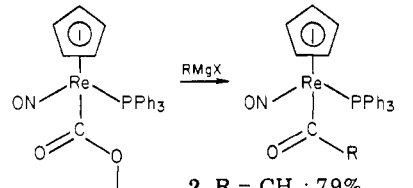
Metal acyl complexes L_nMCOR are a ubiquitous class of compounds. They are known for every transition metal[3] and are particularly common where there exists a readily available metal anion precursor (L_nM^-) which can be acylated[4] or metal alkyl precursor (L_nMR) which can be carbonylated.[5] Metal acyls have also been synthesized via Grignard or alkyllithium attack upon metal carbonyl precursors L_nMCO^{x+} (x = 1, 0, −1), or their equivalents.[3,6]

We have found that a number of remarkably stereospecific ligand-based transformations[7] can be observed with easily resolved[8] chiral (η-C_5H_5)Re(NO)(PPh_3)(X) compounds. Hence, we desired to synthesize a series of chiral rhenium acyls, (η-C_5H_5)Re(NO)(PPh_3)(COR), in order to probe two contemporary aspects of metal acyl chemistry: (1) the conversion of these complexes to cationic vinylidene complexes via the method developed by Hughes[9] and (2) their deprotonation to, among other possible products, metal-substituted enolates.[10] In this paper, we detail the synthesis of nine representative rhenium acyls, (η-C_5H_5)Re(NO)(PPh_3)(COR), including some in optically active form, and describe their reactivity toward the electrophilic reagents BH_3, CH_3SO_3F, and CF_3SO_3H.

Results

Numerous reactions of RMgX and RLi reagents with the cation[11] [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ were attempted. However, conditions for the high-yield synthesis of acyls (η-C_5H_5)Re(NO)(PPh_3)(COR) could not be found. For instance, reaction of [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+$ BF_4^- with C_6H_5Li in CH_2Cl_2 gave benzoyl (η-C_5H_5)Re(NO)(PPh_3)(COC_6H_5) (**5**) in at best 12% yield.[12] We attributed most of this difficulty to homogeneity problems. Cation[(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ is insoluble in Grignard-inert solvents such as hydrocarbons and ethers.

In an alternative approach, cation [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ was first treated with CH_3ONa to give the previously described,[8] benzene-soluble "methyl ester" (η-C_5H_5)Re(NO)(PPh_3)($COOCH_3$) (**1**). When **1** and a variety of Grignard reagents were reacted, acyls (η-C_5H_5)Re(NO)(PPh_3)(COR) (**2**–**9**, eq 1) formed in high yield.



(1)

1

2, R = CH_3; 79%
3, R = CH_2CH_3; 92%
4, R = CH_2-*n*-C_8H_{17}; 74%
5, R = C_6H_5; 91%
6, R = $CH_2C_6H_5$; 66%
7, R = $CH_2CH_2C_6H_5$; 99%
8, R = $CH{=}CH_2$; 77%
9, R = $CH_2CH{=}CH_2$, 82%

Distinctly lower yields of acyls were obtained when **1** was treated with alkyllithium reagents. It was found, however, that acyl (η-C_5H_5)Re(NO)(PPh_3)($COC{\equiv}CCH_3$) (**10**) could be prepared in 48% yield directly from commercial $LiC{\equiv}CCH_3$ and cation [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$. All of the above reactions could be conveniently monitored by TLC.

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(2) To whom correspondence should be addressed at the Univerisity of Utah; Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).
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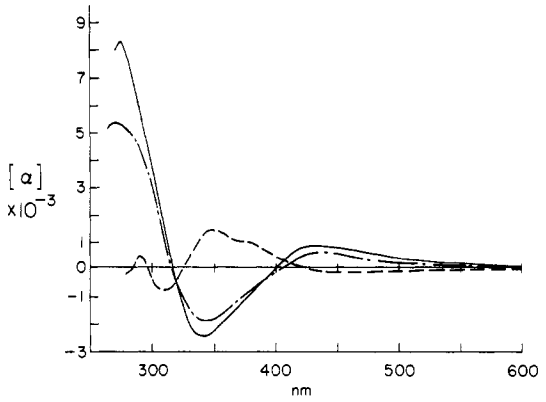


Figure 1. ORD spectra of (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$ ((+)-(*S*)-**2**) (—); (−)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COC_6H_5)$ ((−)-(*S*)-**5**) (- - -); (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_2C_6H_5)$ ((+)-(*S*)-**7**) (· · ·).

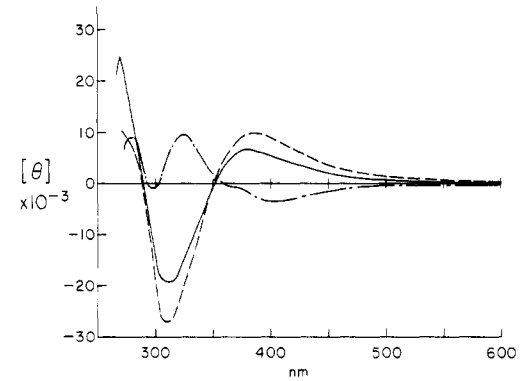


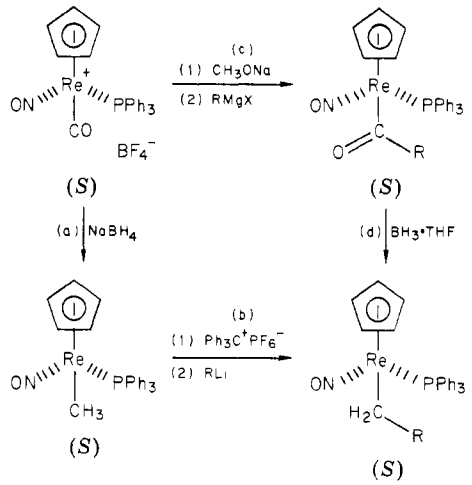
Figure 2. CD spectra of (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$ ((+)-(*S*)-**2**) (- - -); (−)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COC_6H_5)$ ((−)-(*S*)-**5**) (· · ·); (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_2C_6H_5)$ ((+)-(*S*)-**7**) (—).

Acyls **2**–**10** were isolated as yellow to light orange, indefinitely stable powders. They were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, as summarized in Table I, and in some cases by microanalysis, ^{31}P NMR and UV spectroscopy, and mass spectrometry (Experimental Section).

Optically active, 98% ee (−)-(*R*)-**1**[8] was similarly used to prepare optically active acetyl (−)-(*R*)-**2** ($[\alpha]^{24.5}_{589}$ −212°), benzoyl (+)-(*R*)-**5** ($[\alpha]^{24.5}_{589}$ 6.2°), and β-phenylpropionyl (−)-(*R*)-**7** ($[\alpha]^{24.5}_{589}$ −114°).[13] These transformations were also carried out starting with the enantiomer, (+)-(*S*)-**1** (98% ee). Absolute configurations were assigned as described below. ORD and CD spectra are given in Figures 1 and 2.

Relatively recently, it was discovered that BH_3·THF reduces acyclic metal acyls to metal alkyls.[14] Hence, acetyl (−)-(*R*)-**2**, decanoyl **4**, benzoyl (+)-(*R*)-**5**, and β-phenylpropionyl **7** were treated with excess BH_3·THF. Alkyls (−)-(*R*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ ((−)-(*R*)-**11**; $[\alpha]^{24.5}_{589}$ −114°),[8] $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2\text{-}n\text{-}C_8H_{17})$ (**12**), (−)-(*R*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ ((−)-(*R*)-**13**; $[\alpha]^{24.5}_{589}$ −116°),[8] and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)$-$(CH_2CH_2CH_2C_6H_5)$ (**14**) were subsequently isolated in 74–93% yields. The similar BH_3·THF reduction of phenylacetyl **6** to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2C_6H_5)$ has been previously reported.[7d] Acryloyl **8** first underwent C=C reduction to propionyl **3** when treated with BH_3·THF.

Scheme I. A Stereochemical Cycle: Reactions Employed To Establish Absolute Configurations



Absolute configurations were assigned to the optically active rhenium complexes via the following observations and arguments. First, the absolute configuration of the benzyl complex (−)-(*R*)-**13**, prepared via steps a and b in Scheme I (illustrated with the enantiomer), has been established by an X-ray crystal structure.[8] The reactions comprising steps a and b do not involve attack at rhenium and have been assigned as proceeding with retention.[8] Second, Brunner has examined the stereochemistry[6a,15] of several types of nucleophilic attack upon the CO ligand of homologous manganese cation $[(\eta\text{-}C_5H_5)Mn(NO)(PPh_3)(CO)]^+PF_6^-$. His results were most plausibly interpreted as indicating retention at manganese. Finally, the BH_3·THF reduction of formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ has been shown, via a stereochemical cycle, to proceed with >99% retention.[8] Together, these data constitute compelling evidence that steps c and d of Scheme I both proceed with retention at rhenium.

The alkylation of neutral metal acyls to cationic alkoxycarbene complexes has abundant precedent.[16] Hence, acetyl **2** and benzoyl **5** were treated with CH_3SO_3F (eq 2). Workup with $NH_4^+PF_6^-$ gave crystalline $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_3)]^+PF_6^-$ (**15**) and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)C_6H_5)]^+PF_6^-$ (**16**) in 66% and 90% yields, respectively. These compounds were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy as summarized in Table II. The room-temperature ^1H and ^{13}C NMR spectra of **15** and **16** showed only single $\eta\text{-}C_5H_5$, OCH_3, and CH_3 resonances.

Alkylidenes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+$ have been shown to exist as Re=C geometric isomers that undergo nucleophilic attack predominantly from a direction anti to the PPh_3 ligand.[7a,d] In order to aid the assignment of stereochemistry about the Re=C bond of **16**, conversion to the previously described alkyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$[7b] was attempted. Thus **16** was treated with 0.8 equiv of $Li(C_2H_5)_3BH$ at −78 °C. The reaction was then quenched with H_2O to minimize side

(13) (a) Absolute configurations at rhenium are assigned according to the Baird/Sloan modification of the Cahn–Ingold–Prelog priority rules.[13c] The C_5H_5 ligand is considered to be a pseudoatom of atomic number 30, giving the sequence $\eta^5\text{-}C_5H_5$ > PPh_3 > NO > acyl or alkyl. In complexes with more than one chiral center, the rhenium configuration is specified first. (b) Prefixes (+)- and (−)- refer to rotations at 589 nm. (c) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

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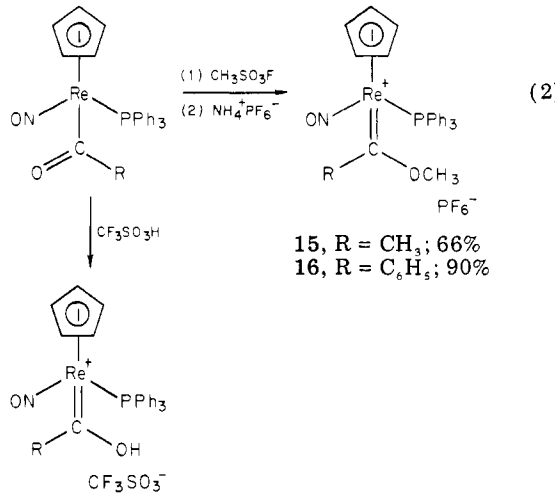

(2)

15, R = CH_3; 66%
16, R = C_6H_5; 90%

17, R = CH_3; 73%
18, R = CH_2CH_3; 91%

reactions, and $(C_6H_5)_3SiCH_3$ standard was added. Analysis of the η-C_5H_5 ^1H NMR resonances indicated the presence of (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$) (27%; see III below),[7b,13] (*SR,RS*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$) (6.5%), (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (19%), and **16** (17%). These data will be interpreted below.

The existence of C--OR geometric isomers in carbene complexes $L_nM{=}C(OR')R$ has also been previously observed.[17] This possibility was probed by variable-temperature NMR. When an acetone-d_6 solution of **15** was cooled to −27 °C, two isomers appeared in a (66 ± 4):(34 ± 4) ratio. Their η-C_5H_5, OCH_3, and CH_3 resonances were at δ 6.01, 4.26, and 2.42 (major isomer) and δ 6.21, 3.85, and 2.70 (minor isomer). The −25 °C ^{13}C NMR spectrum of **15** showed two η-C_5H_5 resonances (97.8 and 98.4 ppm) in a (68 ± 3):(32 ± 3) intensity ratio. When an acetone-d_6 solution of **16** was cooled to −85 °C, no ^1H NMR decoalescence was observed.

Acetone-d_6 solutions of **15** and **16** were irradiated at −78 °C[7b,c,18] and were then rapidly transferred to a −27 °C ^1H NMR probe. The spectra obtained were identical with those noted above.

The protonation of neutral metal acyls to cationic hydroxycarbenes has also been previously observed.[16] Hence, acetyl **2** and propionyl **3** were treated with CF_3SO_3H (eq 2). Workup gave [η-C_5H_5)Re(NO)(PPh_3)(=C(OH)CH_3)]$^+CF_3SO_3^-$ (**17**) and [(η-C_5H_5)Re(NO)(PPh_3)(=C(OH)CH_2CH_3)]$^+CF_3SO_3^-$ (**18**) as yellow solids in 73% and 91% yields, respectively. These compounds were characterized as summarized in Table II. When propionyl **3** was treated with less than 1 equiv of CF_3SO_3H in $CDCl_3$, only one set of ^1H NMR resonances was observed. These resonances were intermediate in chemical shift between **3** and **18** and showed no decoalescence down to −80 °C.

When an acetone-d_6 solution of **17** was cooled to −27 °C, two isomers appeared in a (80 ± 3):(20 ± 3) ratio. The η-C_5H_5 and CH_3 ^1H NMR resonances appeared at δ 6.02 and 2.25 (major isomer) and 6.14 and 2.49 (minor isomer). When an acetone-d_6 solution of **18** was cooled to −27 °C, two isomers appeared in a (95 ± 2):(5 ± 2) ratio. The η-C_5H_5 ^1H NMR resonances were at δ 6.04 and 6.17, respectively.

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Discussion

This study has provided a facile, high-yield route to a variety of rhenium acyls (η-C_5H_5)Re(NO)(PPh_3)(COR). We attribute the success of eq 1 to its homogeneity and use of a Grignard-inert solvent. However, our results must be extrapolated with caution. For instance, Brunner has found that reactions of alkyllithium reagents RLi with [(η-C_5H_5)Mn(NO)(PPh_3)(CO)]$^+PF_6^-$ proceed in high overall yield.[6a] However, the manganese acyl products are accompanied by significant amounts of η^4-C_5H_5R diene complexes formed by RLi attack upon the η-C_5H_5 ligand. Furthermore, reaction of the manganese homologue of **1**, (η-C_5H_5)Mn(NO)(PPh_3)($COOCH_3$), with CH_3MgBr has been reported to give a <2% yield of acetyl (η-C_5H_5)Mn(NO)(PPh_3)($COCH_3$).[19]

Acyls **2–10** exhibit two characteristic spectroscopic features (Table I). The first is an extremely low IR $\nu_{C=O}$ (1558–1493 cm^{-1}), which has also been noted with the formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO).[11] This is a result of the excellent electron-donating ability of the (η-C_5H_5)Re(NO)(PPh_3) moiety. Consequently, zwitterionic $Re^+{=}CRO^-$ resonance forms significantly contribute to the ground states of **2–10**. The second feature is the acyl carbon ^{13}C NMR resonance[20a] observed at 236–256 ppm.

Out of over 30 optically active (η-C_5H_5)Re(NO)(PPh_3)(X) compounds which we have prepared to date,[7e,8] benzoyl (+)-(*R*)-**5** and enantiomer (−)-(*S*)-**5** are the *only* ones whose absolute configurations are not correctly predicted by the sign of the ORD or CD spectrum at >500 nm (or the sign of the region between the two *x* axis crossings). For unknown reasons, their chiroptical properties (Figures 1 and 2) are completely anomolous. The BH_3·THF reduction of (+)-(*R*)-**5** gives benzyl (−)-(*R*)-**13**, which has entirely ordinary chiroptical properties. This constitutes an important caveat regarding the assignment of absolute configurations on the basis of ORD and CD spectra.

The optical rotations of alkyls (−)-(*R*)-**11** and (−)-(*R*)-**13** prepared via steps c and d of Scheme I are approximately 98% of those when the alkyls are prepared via steps a and b. This reflects the small amount of racemization that accompanies the formation of optically active methyl ester **1** (98% ee).[8] Hence the optically active acyls are obtained in 98% ee, and their BH_3·THF reduction must be essentially stereospecific. The specific rotations reported for the optically active acyls should be multiplied by 1.02 to obtain the specific rotations expected for optically pure compounds.

Steps c and d of Scheme I constitute a valuable synthesis of racemic and optically active primary rhenium alkyls. In many cases, we find that overall yields are superior to those realized via alkyllithium attack upon the methylidene [(η-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+PF_6^-$ (steps a and b).

The X-ray crystal structure of formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) shows that the CHO plane is nearly parallel to the Re–NO bond.[11,21] This maximizes overlap of the rhenium d orbital HOMO[7b] with the formyl carbon p orbital. The formyl hydrogen is located syn to the nitrosyl ligand. On this basis, acyl complexes (η-C_5H_5)Re(NO)(PPh_3)(COR) can be expected to have the preferred conformation I (Newman projection down the acyl carbon–rhenium bond). This orients the alkyl substituent

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(20) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981: (a) Table 2.7, (b) Table 2.5.

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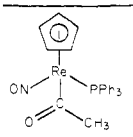
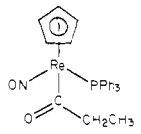
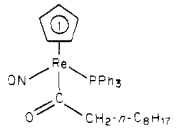
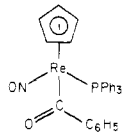
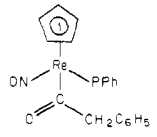
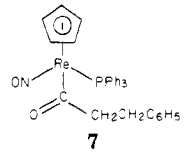
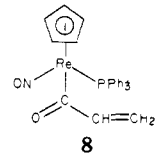
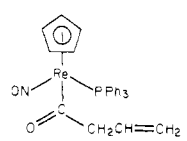
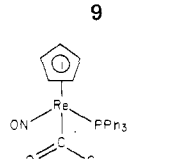
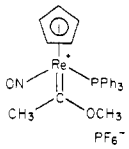
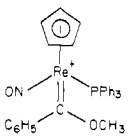
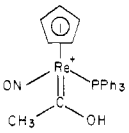
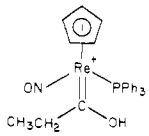
Table I. Spectroscopic Characterization of Rhenium Acyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$

complex	IR (cm^{-1}, $CHCl_3$), $\nu_{N\equiv O}$ and $\nu_{C=O}$	^1H NMR,[a] δ ($CDCl_3$)	^{13}C NMR,[b,c] ppm ($CDCl_3$)		
			ReCOR	C_5H_5	other
 **2**	1658 (s), 1545 (s)	7.53-7.18 (m, 15 H), 5.23 (s, 5 H), 2.03 (s, 3 H)	254.4 (d, J = 8.3 Hz)[c]	93.0 (s)	135.6 (d, J = 55 Hz),[c] 133.6 (d, J = 11.1 Hz), 130.4 (s), 128.3 (d, J = 8.5 Hz), 50.2 (s, CH_3)
 **3**	1652 (s), 1554 (s)	7.54-7.21 (m, 15 H), 5.21 (s, 5 H), 2.56 (m, 1 H), 2.24 (m, 1 H), 0.56 (pseudo t, J = 7 Hz, 3 H)	256.2 (d, J = 9.8 Hz)	92.6 (s)	135.8 (d, J = 53.7 Hz), 133.6 (d, J = 12.2 Hz), 130.4 (s), 128.4 (d, J = 9.8 Hz), 55.9 (s, CH_2), 9.49 (s, CH_3)
 **4**	1651 (s), 1550 (s)	7.75-7.35 (m, 15 H), 5.20 (s, 5 H), 2.66 (d of d of d, J = 15, 9, 6 Hz, 1 H), 2.09 (d of d of d, J = 15, 10, 5 Hz, 1 H), 1.41-0.91 (m, 14 H), 0.88 (t, J = 6 Hz, 3 H)	256.4 (br s)	92.7 (s)	135.7 (d, J = 54.7 Hz), 133.6 (d, J = 10.3 Hz), 130.3 (s), 128.3 (d, J = 10.1 Hz), 63.1 (s, $COCH_2$), 31.9, 2 × 29.7, 2 × 29.4, 25.4, 22.7, 14.1, (s, $n\text{-}C_8H_{17}$)
 **5**	1658 (s), 1514 (s)	7.44-6.84 (m, 20 H), 5.24 (s, 5 H)	256.4 (d, J = 9.5 Hz)[e]	93.1 (s)	157.2, 129.1, 127.7, 127.2 (s, C_6H_5), PPh_3 at 135.7 (d, J = 55.0 Hz), 134.0 (d, J = 11.0 Hz), 130.7 (s), 128.7 (d, J = 10.0 Hz)
 **6**	1652 (s), 1558 (s)	7.58-7.39 (m, 15 H), 7.28-7.01 (m, 5 H), 5.03 (s, 5 H), 4.15 (d, J = 12.8 Hz, 1 H), 3.18 (d, J = 12.8 Hz, 1 H)	251.3 (d, J = 9.2 Hz)	92.5 (s)	137.9, 129.7, 127.8, 125.2 (s, C_6H_5), PPh_3 at 135.7 (d, J = 54.9 Hz), 133.6 (d, J = 11.0 Hz), 130.4 (s), 128.4 (d, J = 11.0 Hz), 69.2 (s, CH_2)
 **7**	1652 (s), 1549 (s)	7.60-6.97 (m, 20 H), 5.13 (s, 5 H), 3.01 (d of d of d, J = 16, 10, 5 Hz, 1 H), 2.72 (d of d of d, J = 15, 9, 5 Hz, 1 H), 2.39 (d of d of d, J = 15, 10, 5 Hz, 1 H), 2.13 (d of d of d, J = 14, 10, 4 Hz, 1 H)	254.9 (br d)	92.7 (s)	143.0, 128.6, 128.1, 125.1 (s, C_6H_5), PPh_3 at 135.6 (d, J = 54.5 Hz), 133.5 (d, J = 10.3 Hz), 130.4 (s), 128.1 (d, J = 7.1 Hz), 64.0 (s, $COCH_2$), 31.5 (s, $CH_2C_6H_5$)
 **8**	1658 (s), 1515 (s)[d]	7.62-7.38 (m, 15 H), 6.56 (d of d, J = 10, 17 Hz, 1 H), 5.26 (s, 5 H), 5.16 (d of d, J = 17, 2 Hz, 1 H), 4.49 (d of d, J = 10, 2 Hz, 1 H)	250.6 (d, J = 9.6 Hz)[e]	93.6 (s)	154.0 (s, CH=),[f] 136.0 (d, J = 55.2 Hz), 134.1 (d, J = 11.0 Hz), 130.9 (s), 128.8 (d, J = 10.9 Hz), 112.6 (s, $=CH_2$)[f]
 **9**	1655 (s), 1520 (s)[d]	7.53-7.41 (m, 15 H), 5.60 (m, 1 H), 5.21 (s, 5 H), 4.88 (d of m, J = 11 Hz), 4.76 (d of m, J = 17 Hz), 3.43 (m, 1 H), 2.82 (m, 1 H)	253.6 (d, J = 9.5 Hz)[e]	93.1 (s)	136.1 (d, J = 55.0 Hz), 135.6 (s, CH=), 134.1 (d, J = 11.0 Hz), 131.0 (s), 128.9 (d, J = 10.9 Hz), 116.0 (s, $=CH_2$),[f] 68.1 (s, CH_2)
 **10**	1675 (s), 1496 (s)[g]	7.54-7.23 (m, 15 H), 5.28 (s, 5 H), 1.88 (s, 3 H)	236.6 (d, J = 11.0 Hz)	93.5 (s)	134.9 (d, J = 50.5 Hz), 133.6 (d, J = 8.8 Hz), 130.4 (s), 128.3 (d, J = 10.9 Hz), 91.9 and 89.5 (s, C≡C), 4.19 (s, CH_3)

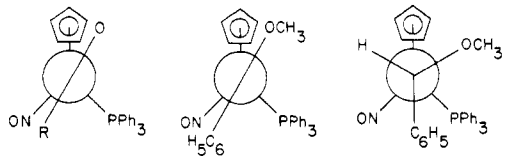
[a] At 200 MHz unless noted. [b] At 50 MHz unless noted. [c] All couplings (J) are to ^{31}P. [d] In CH_2Cl_2. [e] At 75 MHz. [f] Assignments based on the ^1H coupled spectrum, obtained with the gated decoupler on during the pulse delay and off during acquisition. [g] $\nu_{C\equiv C}$ 2183 (w) cm^{-1}.

Table II. Spectroscopic Characterization of Rhenium Carbenes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OR')R)]^+X^-$

complex	IR, cm^{-1} (KBr)	^1H NMR,[a] δ (acetone-d_6)	^{13}C NMR,[b,c] ppm		
			$Re^+=C$	C_5H_5	other
 15	3117-2847 (w), 1697 (vs) ($\nu_{N\equiv O}$) 1588 (w), 1574 (w), 1483 (m), 1461 (m), 1437 (s), 1423 (m), 1351 (m), 1313 (w), 1265 (s br), 1193 (m), 1163 (w), 1118 (m), 1097 (s), 1002 (m), 930 (w), 840 (vs vbr), 750 (s), 710 (m), 696 (s)	7.81-7.30 (m, 15 H), 5.99 (br s, 5 H), 4.12 (br s, 3 H), 2.55 (s, 3 H)	300.6 (br s)[d,e]	98.0 (s)	134.6 (d, J = 10.9 Hz),[c] 133.4 (s), 133.3 (d, J = 59.4 Hz), 130.8 (d, J = 10.9 Hz), 63.7 (s, OCH_3), 40.4 (s, CH_3)[f]
 16	3115 (w), 3068 (w), 2942 (w), 2840 (w), 1718 (vs) ($\nu_{N\equiv O}$), 1594 (w), 1575 (w), 1484 (m), 1437 (s), 1424 (m), 1259 (m br), 1193 (m), 1151 (s), 1134 (m), 1096 (m), 1074 (m), 1061 (m), 998 (m), 953 (m), 925 (m), 840 (vs vbr), 769 (m), 751 (m), 705 (m), 694 (m), 664 (m)	8.10-7.16 (m, 18 H), 6.82-6.72 (m, 2 H), 6.08 (br s, 5 H), 3.99 3.99 (br s, 3 H)	298.2 (br s)[d]	98.3 (s)	149.4, 133.3, 129.4, 126.5 (s, C_6H_5), PPh_3 at 134.5 (d, J = 11.9 Hz), 132.6 (d),[g] 132.1 (s), 130.8 (d, J = 12.1 Hz), 66.0 (s, OCH_3)
 17	3280-2320 (m br), 1697 (vs) ($\nu_{N\equiv O}$), 1485 (m), 1437 (m), 1424 (m), 1351 (m), 1295 (vs), 1231 (vs), 1218 (vs), 1175 (s), 1162 (s), 1095 (s), 1022 (s), 1001 (m), 977 (m), 857 (m), 831 (m), 754 (m), 708 (m), 695 (s), 637 (s), 611 (w)	7.74-7.25 (m, 15 H), 5.94 (s, 5 H), 2.35 (s, 3 H)[h,i]	298.1 (s)[j]	96.3 (s)	133.6 (d, J = 12.5 Hz), 132.8 (d, J = 62.6 Hz), 132.5 (s), 129.8 (d, J unresolved), 44.4 (s, CH_3)
 18	3280-2280 (m br), 1702 (vs) ($\nu_{N\equiv O}$), 1484 (m), 1437 (s), 1424 (m), 1303 (vs), 1225 (vs), 1211 (vs), 1168 (s), 1161 (s), 1096 (s), 1053 (m), 1024 (s), 1013 (s), 998 (m), 924 m, 850 (m), 831 (m), 751 (m), 744 (m), 709 (m), 695 (s), 638 (s)	7.79-7.30 (m, 15 H), 5.96 (s, 5 H), 1.00 (t, J = 7.7 Hz, 3 H)[h,k]	303.2 (s)[j]	96.2 (s)	133.5 (d, J = 12.5 Hz), 132.5 (d, J = 56.3 Hz), Hz), 132.5 (s), 129.9 (d, J = 12.5 Hz), 50.7 (s, CH_2), 12.1 (s, CH_3)

[a] At 80 MHz, 29 °C. [b] At 75 MHz, 29 °C unless noted. [c] All couplings (J) are to ^{31}P. [d] In acetone-d_6. [e] At 40 °C. [f] The CH_3 resonance is broadened by exchange between 25 and 40 °C; this chemical shift is that of the major isomer present at −25 °C. [g] High-field line of PPh_3 *ipso* carbon doublet; other line obscured. [h] No OH resonances were observed in acetone-d_6 (δ 0-12) or $CDCl_3$ (δ 0-23). [i] Data in $CDCl_3$ δ 5.59 (s, 5 H), 2.31 (s, 3 H). [j] In $CDCl_3$, 6.26 Hz/point. [k] Methylene protons not clearly resolved; data in $CDCl_3$: δ 5.61 (s, 5 H), 2.95-2.18 (m, 2 H), 0.98 (t, J = 7.5 Hz, 3 H).

away from the bulky PPh_3 and medium-sized η-C_5H_5 ligands.



I II III

The assignment of preferred conformations to acyl methylation and protonation products, alkoxy- and hydroxycarbenes **15–18**, is somewhat problematic. Rotational barriers about Re=CHR bonds have been found to be 19–22 kcal/mol (ΔG^*_{298}).[7b,d] The donor substituent in Re=C(OR')R complexes may slightly weaken the Re=C bond. However, formyl methylation and protonation products, methoxycarbene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)H)]^+SO_3F^-$ and hydroxycarbene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OH)H)]^+CF_3SO_3^-$, exist as ca. 95:5 and 50:50 mixtures of Re=C geometric isomers, respectively. No evidence has ever been observed for rapid interconversion of Re=C geometric isomers on the NMR time scale. We therefore assume that the room-temperature ^1H NMR spectra of **15–18** accurately indicate their Re=C geometric isomer ratios (>98:<2).

As mentioned, a variety of alkyl and hydride nucleophiles have been shown to rapidly attack alkylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+PF_6^-$ at −78 °C from a direction predominantly (90:10 to >99:1) anti to the PPh_3 ligand. We reason that methoxycarbene **16** should behave similarly. One rotamer of the major product of the reaction of **16** with $Li(C_2H_5)_3BH$, (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$), is shown in Newman projection III. Hence, **16** likely has the synclinal[7b,d] structure depicted in Newman procection II. This experiment, however, deserves cautious interpretation, since an appreciable amount of further reduction to (η-C_5H_5)-Re(NO)(PPh_3)($CH_2C_6H_5$) also occurs. Nonetheless, even in the unlikely event that this reduction occurs *entirely* via the opposite diasteromer—(*SR,RS*)-(η-C_5H_5)Re-(NO)(PPh_3)($CH(OCH_3)C_6H_5$)—(*SS,RR*)-(η-C_5H_5)Re-(NO)(PPh_3)($CH(OCH_3)C_6H_5$) would still constitute the principal initial product.

We propose that **15** also exists in a conformation similar to II. Both phenyl and methyl present a greater steric demand than methoxy,[22] and it is unlikely that the pre-

(22) (a) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 130. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

ferred orientation of Re=C substituents entirely reverses upon substituting phenyl by methyl. We also propose that hydroxycarbenes **17** and **18** exist with their alkyl and hydroxy substituents oriented as in II. However, as noted above, replacement of the alkyl substituents in **17** and **18** by hydrogen makes the two Re=C geometric isomers of nearly equal energy.

Fischer has shown that the carbene $(CO)_5Cr{=}C(OCH_3)CH_3$ exists, depending upon solvent, as a 90–50:10–50 mixture of C–OCH$_3$ isomers.[17a] In acetone-d_6, the activation energy for isomer interconversion was found to be 12.4 ± 1.0 kcal/mol. Similar results were obtained with a series of phenyl-substituted complexes $(CO)_5Cr{=}C(OCH_3)C_6H_4X$.[17b] In nearly all cases, coalescence of the C–OCH$_3$ isomer ^{1}H NMR resonances was observed between −37 and 4 °C. We suggest that the ^{1}H NMR behavior of **15**, **17**, and **18** upon cooling is due to similar C–OR′ isomers. It is worth noting that at −78 °C, hydroxycarbene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OH)H)]^+CF_3SO_3^-$ exists as a mixture of *four* (Re=C and C–OH) isomers.[11]

Finally, it should be emphasized that it is exceedingly difficult to unambiguously determine the lowest energy conformations of the methoxycarbene and hydroxycarbene ligands in **15–18**. Even X-ray crystal structures would not necessarily reflect the preferred solution Re=C and C–OR geometries.

Alkoxycarbene and hydroxycarbene complexes have a rich chemistry.[16,23,24] The latter are generally somewhat labile.[16,23] The first hydroxycarbene complex to be isolated in pure form was $(\eta\text{-}C_5H_5)Re(CO)_2(=C(OH)CH_3)$,[23a] which is a close relative of **17**. Complexes **15–18** exhibit the expected[20b] carbene carbon ^{13}C NMR resonances (Table II). The OH resonance was not detected in the ^{1}H NMR spectra of hydroxycarbene complexes **17** and **18**. However, both compounds show a broad featureless absorbance from 3280 to ca. 2300 cm^{-1} in their IR spectra, which we assign as $\nu_{O\text{-}H}$.[23b]

In conclusion we have developed a facile general route to rhenium acyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ and have examined several fundamental aspects of their chemistry. Novel and useful transformations involving these acyls will be reported in the near future.

Experimental Section

General Remarks. All reactions were carried out under an inert atmosphere. Solvents were dried and deoxygenated as previously described.[7b,d,e] Racemic[11] and optically active[8] $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ were prepared by published procedures. Reagents CH_3MgBr (3.0 M in ether), CH_3CH_2MgBr (3.0 M in ether), $H_2C{=}CHMgBr$ (1.0 M in THF), $H_2C{=}CHCH_2MgBr$ (1.0 M in THF), $BH_3{\cdot}THF$ (1.0 M in THF), and Li$(C_2H_5)_3BH$ (1.0 M in THF) were purchased from Aldrich. Grignards $n\text{-}C_8H_{17}CH_2MgBr$, C_6H_5MgBr, and $C_6H_5CH_2CH_2MgBr$ were prepared by standard methods.[25] Reagents $C_6H_5CH_2MgCl$ (1.8 in THF), $LiC{\equiv}CCH_3$, and $NH_4^+PF_6^-$ were obtained from Alfa. All RMgX and RLi reagents were used without standardization. Electrophiles CH_3SO_3F and CF_3SO_3H were obtained from Aldrich and were distilled prior to use. Silane $(C_6H_5)_3SiCH_3$ was prepared from $(C_6H_5)_3SiCl$ and CH_3MgBr analogously to the literature procedure.[26] Photolyses were conducted as previously described.[7b,18]

NMR data other than in the tables were obtained as follows: ^{13}C NMR, Varian SC-300, referenced to internal $(CH_3)_4Si$; ^{1}H and ^{31}P NMR, Varian FT-80, referenced to internal $(CH_3)_4Si$ and external 85% H_3PO_4, respectively. IR spectra were recorded in Perkin-Elmer Model 521 and 1500 (FT) spectrometers. UV spectra were recorded on a Cary 219 spectrometer. Mass spectra were obtained on a AEI-MS9 instrument. Microanalyses were conducted by Galbraith.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COOH_3)$ (1). Both the literature synthesis[8] and the following procedure were employed. A 200-mL flask was charged with 1.91 g (2.90 mmol) of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$, 75 mL of CH_2Cl_2, and a stir bar. The resulting yellow solution was cooled to −78 °C, and 0.80 g (15 mmol) of $NaOCH_3$ in 30 mL of CH_3OH was added. The reaction mixture was stirred at −78 °C for 20 min and then allowed to warm to room temperature. After an additional 0.5 h, solvent was removed under reduced pressure. The resulting yellow solid was extracted with toluene, and the extract was filtered through a coarse porosity glass frit. The toluene was removed and the yellow solid vacuum dried to give 1.79 g (2.90 mmol, 100%) of **1**. The ^{1}H NMR spectrum was identical with that of an authentic sample.[8]

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$ (2). A 200-mL Schlenk flask was charged with 1.80 g (2.9 mmol) of **1**, 100 mL of toluene, and a stir bar. Then 1.5 mL of CH_3MgBr (3.0 M in ether) was added, and the reaction mixture was stirred for 0.5 h. The solvents were removed under reduced pressure, and the resulting yellow residue was extracted with acetone. The extract was filtered through silica gel, and the acetone was removed to give a yellow solid which was washed with 5 mL of acetone and vacuum dried. Thus obtained was 1.35 g (2.30 mmol, 79%) of **2**: mp 197–202 °C dec; $^{31}P\{^1H\}$ NMR (ppm, benzene-d_6) 16.72 (s); mass spectrum (16 eV), m/e (relative intensity) 587 (M^+, ^{187}Re, 2), 572 ($M^+ - CH_3$, 100); UV (nm, $CHCl_3$) 268 (pk ϵ 3800), 288 (sh, ϵ 2400). Anal. Calcd for $C_{25}H_{23}NO_2PRe$: C, 51.18; H, 3.95; N, 2.39; P, 5.28. Found: C, 51.48; H, 4.12; N, 2.24; P, 5.14.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_3)$ (3). This compound was prepared from 2.9 mmol of **1** and 2.0 mL of CH_3CH_2MgBr (3.0 M in ether) in a manner identical with that for **2**. Thus obtained was 1.60 g (2.67 mmol, 92%) of **3**, mp >220 °C.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2\text{-}n\text{-}C_8H_{17})$ (4). This compound was prepared from 0.0332 mmol of **1** and 0.88 mL of $n\text{-}C_8H_{17}CH_2MgBr$ (0.75 M in Et_2O) in a manner similar to that for **2**. After the acetone extract was filtered through silica gel, solvent was removed to give a yellow oil. This oil was dissolved in benzene. Hexanes were added, and the mixture was kept at −25 °C for 1 day. Product **4** precipitated as a yellow powder which was collected by filtration and vacuum dried (0.171 g, 0.245 mmol, 74%); mp 104 °C.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COC_6H_5)$ (5). A synthesis of **5** (12%) from $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ and C_6H_5Li has been communicated.[12] It is best prepared by a procedure analogous to the one given below for (+)-(*R*)-**5**. Data: mp 198–202 °C dec; mass spectrum (70 eV), *m/e* (relative intensity) 649 (M^+, ^{187}Re, 10), 572 ($M^+ - C_6H_5$, 83), 544 ($M^+ - COC_6H_5$, 47), 262 (PPh_3, 100); UV (nm, $CHCl_3$) 265 (pk, ϵ 4300), 295 (sh, ϵ 2200). When **5** was recrystallized from toluene/hexane, orange crystals of the solvate **5**·(toluene)$_{0.4}$ were reproducibly obtained. Calcd for $C_{30}H_{25}NO_2PRe + (C_7H_8)_{0.4}$: C, 57.47; H, 4.15; N, 2.04; P, 4.52. Found: C, 57.64; H, 4.25; N, 2.39; P, 4.47.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2C_6H_5)$ (6). This compound was prepared from 2.9 mmol of **1** and 8.0 mL of $C_6H_5CH_2MgCl$ (1.8 M in THF) in a manner similar to that for **2**. After the acetone extract was filtered through silica gel, it was concentrated to 20 mL. Then 5 mL of hexane was added, and the solution was cooled to −20 °C. Orange crystals of **6** formed, which after 24 h were collected by filtration and vacuum dried (1.26 g, 1.90 mmol, 66%); mp >220 °C.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_2C_6H_5)$ (7). A 250-mL Schlenk flask was charged with 0.900 g (1.52 mmol) of **1**, 75 mL of THF, and a stir bar. Then 3 equiv of $C_6H_5CH_2CH_2MgBr$ (freshly prepared from 4.56 mmol of the alkyl bromide in 50 mL of ether) was added, and the reaction mixture was stirred for 5 h. The solvents were removed under reduced pressure, and the resulting yellow residue was extracted with acetone. The

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extract was filtered through silica gel, and the acetone was removed to give a yellow solid. Yellow crystals of **7** were obtained from benzene/hexanes (1.01 g, 1.52 mmol, >99%); mp 204–205 °C; $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 0 °C) 16.12 (s); mass spectrum (70 eV), *m/e* (relative intensity) 572 ($M^+ - CH_2CH_2C_6H_5$, ^{187}Re, 100), 544 ($M^+ - COCH_2CH_2C_6H_5$, 31), no M^+ at 16 eV; UV (nm, $CHCl_3$) 265 (pk ϵ 3000), 288 (sh, ϵ 1700).

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($COCH{=}CH_2$) (8). This compound was prepared from 2.9 mmol of **1** and 8.7 mL of $H_2C{=}CHMgBr$ (1.0 M in THF) in a manner similar to that for **2**. After the acetone extract was filtered through silica gel, solvent was removed to give the crude yellow product (1.34 g, 2.24 mmol, 77%). Orange crystals of **9** were obtained from CH_2Cl_2/hexane (1.00 g, 1.67 mmol, 58%); mp 210–215 °C.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($COCH_2CH{=}CH_2$) (9). This compound was prepared from 2.9 mmol of **1** and 8.7 mL of $H_2C{=}CHCH_2MgBr$ (1.0 M in THF) in a manner similar to that for **2**. After the acetone extract was filtered through silica gel, solvent was removed to give the crude yellow product (1.45 g, 2.37 mmol, 82%). Orange crystals of **9** were obtained from CH_2Cl_2/hexane (0.98 g, 1.60 mmol, 55%); mp 202–203 °C.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($COC{\equiv}CCH_3$) (10). A 200-mL Schlenk flask was charged with 0.50 g (0.76 mmol) of [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$, 50 mL of dry THF, and a stir bar. To the resulting suspension was added 0.048 g (1.04 mmol) of $LiC{\equiv}CCH_3$, and the reaction was allowed to stir overnight. Solvent was then removed under reduced pressure from the resulting orange solution. The residue was extracted with ca. 100 mL of toluene. The extract was filtered, was concentrated to ca. 20 mL, and was flooded with hexane. The resulting off-white solid was removed by filtering through a medium porosity frit. The orange filtrate was taken to dryness under vacuum. This yielded an orange oil which gave **10** as a yellow powder (0.22 g, 0.361 mmol, 48%), mp 140–150 °C dec, from 80:20 CH_2Cl_2/hexane.

Preparation of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($COCH_3$) ((–)-(*R*)-2). A 100-mL Schlenk flask was charged with 0.215 g (0.359 mol) of 98% ee (–)-(*R*)-**1**, 30 mL of CH_2Cl_2, and a magnetic stir bar. Then 0.180 mL of CH_3MgBr (3.0 M in ether) was slowly added, and the reaction was stirred for 0.25 h. The solvents were removed under oil pump vacuum. The resulting yellow residue was extracted with acetone. The extract was filtered through silica gel, and the solvent was removed under vacuum. The resulting yellow solid was recrystallized from CH_2Cl_2/hexane to give 0.197 g (0.337 mmol, 94%) of (–)-(*R*)-**2**: mp 225–228 °C dec; $[\alpha]^{24.5}_{589}$ –212° (*c* 0.41, $CHCl_3$). The enantiomer (+)-(*S*)-**2** was prepared identically from (+)-(*S*)-**1**.

Preparation of (+)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(COC_6H_5) ((+)-(*R*)-5). A 100-mL Schlenk flask was charged with 0.212 g (0.352 mmol) of 98% ee (–)-(*R*)-**1**, 30 mL of CH_2Cl_2, and a magnetic stir bar. Then 0.315 mL of C_6H_5MgBr (1.7 M in ether) was slowly added, and the reaction was stirred for 0.25 h. The solvents were removed under oil pump vacuum. The resulting yellow residue was extracted with acetone. The extract was filtered through silica gel, and the solvent was removed under vacuum. The resulting yellow solid was triturated with hexanes to give 0.211 g (0.325 mmol, 91%) of (+)-(*R*)-**5**: mp 182–184 °C dec; $[\alpha]^{24.5}_{589}$ 6.2° (*c* 0.35, $CHCl_3$). The enantiomer (–)-(*S*)-**5** was prepared identically from (+)-(*S*)-**1**.

Preparation of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($COCH_2CH_2C_6H_5$) ((–)-(*R*)-7). This compound was prepared from 0.350 mmol of (–)-(*R*)-**1** and 0.525 mL of $C_6H_5CH_2CH_2MgBr$ (1.0 M in ether) in a manner identical with that for (+)-(*R*)-**5**. Thus obtained was 0.211 g (0.312 mmol, 89%) of (–)-(*R*)-**7**: mp 114–115 °C; $[\alpha]^{24.5}_{589}$ –144° (*c* 0.36, $CHCl_3$). The enantiomer (+)-(*S*)-**7** was prepared identically from (+)-(*S*)-**2**.

Preparation of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) ((–)-(*R*)-11). A 100-mL Schlenk flask was charged with 0.238 g (0.406 mmol) of (–)-(*R*)-**2** and 30 mL of THF and fitted with a reflux condensor. Then 2.03 mL of BH_3·THF (1.0 M in THF) was added, and the mixture was refluxed for 4 h. The reaction was allowed to cool. Then 2 mL of CH_3OH was added, and the solvent was removed by rotary evaporation. The orange residue was dissolved in benzene and filtered through silica gel. The solvent was removed from the filtrate by rotary evaporation, and the orange solid was recrystallized from CH_2Cl_2/hexane to give 0.213 g (0.374 mmol, 92%) of (–)-(*R*)-**11**: mp 179–180 °C; $[\alpha]^{24.5}_{589}$ –114° ($CHCl_3$) (lit.[8] –116°). The enantiomer (+)-(*S*)-**11** was prepared identically from (+)-(*S*)-**2**.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)(CH_2CH_2-*n*-C_8H_{17}) (12). This compound was prepared from 0.0855 g (0.122 mmol) of **4** in 50 mL of THF and 2.40 mL of BH_3·THF (1.0 M in THF) in a manner similar to that for (–)-(*R*)-**11**. The orange residue obtained after the CH_3OH quench was chromatographed on silica gel in benzene. The orange fraction was collected, concentrated to a solid, and precipitated from cold hexane to give 0.062 g (0.091 mmol, 74%) of **12** as an orange powder: mp 82 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1620 (s); ^1H NMR (δ, $CDCl_3$) 7.40–7.30 (m, 15 H), 4.89 (s, 5 H) 2.18–1.96 (m, 1 H), 1.79–1.62 (m, 3 H), 1.35–1.18 (m, 14 H), 0.89 (t, J = 6 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) PPh_3 at 136.8 (d, $J_{^{13}C-^{31}P}$ = 51.3 Hz), 133.7 (d, J = 9.8 Hz), 129.8 (s), 128.2 (d, J = 9.8 Hz), 89.5 (s, C_5H_5), 41.8, 35.7, 32.0, 29.9, 29.8, 29.5, 29.4, 22.7 (s, CH_2), 14.1 (s, CH_3), –9.2 (d, $J_{^{13}C-^{31}P}$ = 4.9 Hz, $ReCH_2$).

Preparation of (–)-(*R*)-(η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) ((–)-(*R*)-13). This compound was prepared from 0.228 g (0.352 mmol) of (+)-(*R*)-**5** and 1.76 mL of BH_3·THF (1.0 M in THF) in a manner identical with that for (–)-(*R*)-**11**. The CH_2Cl_2/hexane recrystallization gave 0.119 g (0.313 mmol, 89%) of (–)-(*R*)-**13**: mp 234–237 °C dec; $[\alpha]^{24.5}_{589}$ –116° ($CHCl_3$) (lit.[8] –118°). The enantiomer (+)-(*R*)-**13** was prepared identically from (–)-(*S*)-**5**.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($CH_2CH_2CH_2C_6H_5$) (14). This compound was prepared from 1.01 g (1.49 mmol) of **7** in 300 mL of THF and 30.4 mL of BH_3·THF (1.0 M in THF) in a manner similar to **12**. The orange fraction from the silica gel column was concentrated to a solid and precipitated from cold benzene/hexane to give 0.917 g (1.39 mmol, 93%) of **14** as an orange powder: mp 151–152 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1623 (s); ^1H NMR (δ, $CDCl_3$) 7.43–7.10 (m, 20 H), 4.88 (s, 5 H), 2.65–2.36 (m, 2 H), 2.22–1.93 (m, 3 H), 1.83–1.70 (m, 1 H); ^{13}C NMR (ppm $CDCl_3$) 144.0, 128.5, 128.0, 125.0 (s, C_6H_5), PPh_3 at 136.6 (d, $J_{^{13}C-^{31}P}$ = 51.3 Hz), 133.6 (d, J = 9.8 Hz), 129.9 (s), 128.2 (d, J = 9.8 Hz), 89.5 (s, C_5H_5), 43.9, 42.1 (s, CH_2), –9.4 (br s, $ReCH_2$).

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)-CH_3)]$^+PF_6^-$ (15). A 50-mL Schlenk flask was charged with 0.250 g (0.427 mmol) of **2**, 25 mL of CH_2Cl_2, and a stir bar. Then 50 μL (0.067 g, 0.59 mmol) of CH_3SO_3F was added by syringe, and the resultant yellow solution was stirred for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in 10 mL of acetone. Then 0.695 g (4.27 mmol) of $NH_4^+PF_6^-$ was added. This solution was stirred for 30 min, after which the acetone was removed under reduced pressure. The residue was extracted with $CHCl_3$ and filtered. Diffusion addition of ether to the filtrate gave yellow needles of **15** (0.209 g, 0.281 mmol, 66%), mp 177–195 °C dec.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=C-(OCH_3)C_6H_5)]$^+PF_6^-$ (16). This compound was prepared from 0.250 g (0.386 mmol) of **5**, 40 μL (62 mg, 0.54 mmol) of CH_3SO_3F, and 0.629 g (3.86 mmol) of $NH_4^+PF_6^-$ in a manner identical with that for **15**. Carbene **16** was obtained as irregular yellow-gold crystals (0.280 g, 0.346 mmol, 90%), mp 177–198 °C dec. Anal. Calcd for $C_{31}H_{28}F_6NO_2P_2Re$: C, 46.02; H, 3.49; N, 1.73; P, 7.66. Found: C, 45.89; H, 3.62; N, 1.79; P, 7.47.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=C(OH)CH_3)]$^+$ $CF_3SO_3^-$ (17). A 50-mL Schlenk flask was charged with 0.244 g (0.417 mmol) of **2**, 25 mL of CH_2Cl_2, and a stir bar. Then 41 μL (0.069 g, 0.46 mmol) of CF_3SO_3H was added by syringe, and the resultant light yellow solution was stirred for 1 h. The solvent was removed, and the residue was extracted with $CHCl_3$. The extract was filtered. Diffusion addition of ether to the filtrate gave **17** as a yellow-gold semicrystalline solid (0.223 g, 0.303 mmol, 73%), mp 180–181 °C dec.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=C(OH)C_2H_5)]$^+$ $CF_3SO_3^-$ (18). This compound was prepared from 0.250 g (0.417 mmol) of **3** and 41 μL (0.069 g, 0.46 mmol) of CF_3SO_3H in a manner identical with that from **17**. Hydroxycarbene **18** was obtained as a dull yellow semicrystalline solid (0.285 g, 0.380 mmol, 91%), mp 180–181 °C dec.

Reaction of 16 with $Li(C_2H_5)_3BH$. A 50-mL Schlenk flask was charged with 25.0 mg (0.0309 mmol) of **16**, 5 mL of CH_2Cl_2, and a stir bar. The yellow solution was cooled to –78 °C, and 25 μL (0.0250 mmol) of $Li(C_2H_5)_3BH$ (1.0 M in THF) was added by syringe. The resulting orange solution was stirred for 10 min at –78 °C, and then 1 mL of H_2O was added. The solvents were then

removed under vacuum below 0 °C. This gave an orange solid residue to which 8.5 mg (0.0309 mmol) of $(C_6H_5)_3SiCH_3$ standard was added. The mixture was extracted with $CDCl_3$, $(CH_3)_4Si$ was added, and the ^1H NMR yields given in the results section were obtained. The ^1H NMR resonances utilized were as followed: **16**, δ 5.79;[12] (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$), δ 4.89 and 2.67;[7b] (*SR,RS*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$), δ 4.65 and 2.55;[7b] (η-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) δ 4.73.[7b]
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Registry No. 1, 82293-79-6; (−)-(*R*)-1, 82336-22-9; (+)-(*S*)-1, 87480-09-9; 2, 82582-46-5; (−)-(*R*)-2, 87412-37-1; (+)-(*S*)-2, 87480-06-6; 3, 82582-47-6; 4, 87412-24-6; 5, 76770-59-7; (−)-(*S*)-5, 87480-05-5; (+)-(*R*)-5, 87480-04-4; 6, 82582-48-7; 7, 87412-25-7; (−)-(*R*)-7, 87480-07-7; (+)-(*S*)-7, 87480-08-8; 8, 87412-26-8; 9, 87412-27-9; 10, 87412-28-0; (−)-(*R*)-11, 82336-34-3; (+)-(*S*)-11, 82336-35-4; 12, 87412-29-1; 13, 71763-28-5; (−)-(*R*)-13, 82336-32-1; (+)-(*S*)-13, 82336-33-2; 14, 87412-30-4; 15, 87412-32-6; 16, 76770-58-6; 17, 87412-34-8; 18, 87412-36-0; (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$), 76770-56-4; (*SR,RS*)-(η-C_5H_5)Re(NO)(PPh_3)($CH(OCH_3)C_6H_5$), 76821-65-3.

Preparation and Properties of Dibismuthines

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Tetramethyldibismuthine, **1**, tetraisopropenyldibismuthine, **15**, 1,1′-bibismolane, **16**, and tetrakis(2-methyl-1-propenyl)dibismuthine, **17**, have been prepared from the reaction of the corresponding tertiary bismuthines with sodium in liquid ammonia followed by treatment with 1,2-dichloroethane. Tetraphenyldibismuthine, **4**, was prepared by an analogous route from diphenylbismuth chloride. While all the dibismuthines are red in solution, **1**, **15**, and **16** freeze to blue solids. Compounds **4** and **17** form red solids. The Raman, UV, and mass spectra of the dibismuthines are discussed. The dibismuthines thermally decompose to form bismuth metal and corresponding tertiary bismuthine. The reactions of tetramethyldibismuthine with iodine, bromotrichloromethane, benzyl bromide, hydrochloric acid, and butyllithium have been explored. The reactions afford products in which the Bi–Bi bond has been cleaved.

Introduction

Although tetramethyldibismuthine, **1**, was reported in 1935,[1] the intervening years have seen little sustained interest in compounds containing bismuth–bismuth bonds.[2-4] This situation changed abruptly in 1982 with reports of the synthesis of tetrakis(trimethylsilyl)dibismuthine, **2**,[5] tetraethyldibismuthine, **3**,[6] and a reinvestigation of tetramethyldibismuthine.[7] More recently, tetraphenyldibismuthine, **4**,[8] and a series of tetraalkyldibismuthines, **5**, **6**, and **7**,[9] have been characterized.

Me_4Bi_2 (**1**) $(Me_3Si)_4Bi_2$ (**2**) Et_4Bi_2 (**3**)

Ph_4Bi_2 (**4**) R_4Bi_2 **5**, R = Pr; **6**, R = Bu; **7**, R = *i*-Pr

The major reason for this renaissance of interest in dibismuthine chemistry has been the hope that dibismuthines might show the same dramatic thermochromic effects which have been observed for distibines. For example, the distibine tetramethylbistibolyl, **8**, forms blue crystals which melt reversibly to a yellow oil. A crystal structure of **8** shows that the Sb atoms are aligned in linear chains with very short "intermolecular" Sb···Sb contacts.[10] Apparently the solid-phase color is associated with this extended bonding along the Sb–Sb···Sb–Sb chains.[11] Similar thermochromic effects are found for tetramethyldistibine, **9**,[1] tetrakis(trimethylsilyl)distibine, **10**,[12,13] tetraisopropenyldistibine, **11**,[14] and bistibolane, **12**.[15] Crystal structures show that **9**[16] and **10**[13] have intermolecular association similar to that of **8**. On the other hand, distibines such as tetraphenyldistibine, **13**,[17] and tetra-

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