theoretical investigation of the relationship between carbon NMR shifts and element–carbon multiple bonding would be helpful.

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Registry No. 3, 97102-15-3; 4, 97102-16-4; 8, 821-10-3; 10, 7572-29-4; 11, 97102-17-5; $C_6H_5AsCl_2$, 696-28-6; $C_6H_5SbCl_2$, 5035-52-9.

Reactions of Chiral (α-Methoxyvinyl)rhenium Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$ with Alkyl Halides. Efficient 1,3-Asymmetric Induction

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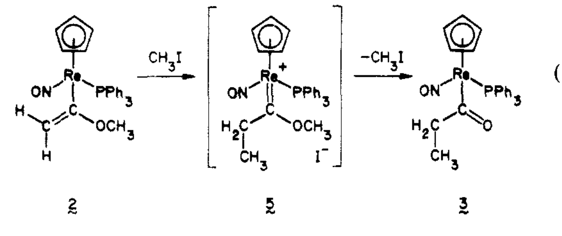
Summary: α-Methoxyvinyl complexes (Z)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$ are readily alkylated ($C_6H_5CH_2Br$, CH_3I) to give acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCHRR')$ with high diastereoselectivity; the stereochemistry of these reactions, and probable transition-state geometries, are established by an X-ray crystal structure of the product (SR,RS)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)CH_2C_6H_5)$.

We recently described the synthesis of chiral vinylrhenium complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$.[1] These reacted with strong electrophiles (E^+X^-) such as CH_3SO_3F to give alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCHRE)]^+X^-$ containing a new asymmetric carbon. Although excellent 1,3-asymmetric induction was achieved, the synthetic utility of this chemistry was limited by the modest nucleophilicity of the vinyl complexes. At that time, we proposed that an α-oxygen substituent might provide enhanced reactivity and consequently broader applicability of this chemistry in asymmetric synthesis. In this communication, we report the successful realization of these goals with α-methoxyvinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$. Similar observations have also been communicated by Davies with related iron complexes.[2]

Treatment of methoxycarbene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_3)]^+PF_6^-$ (1) with NaH (THF, 25 °C) gave, after workup, α-methoxyvinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CH_2)$ (2)[4] in 75% yield. Reaction of 2 with CH_3I (CH_2Cl_2, 12 h) occurred readily at room temperature to give propionyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_3)$ (3, eq 1)[3] and lesser quantities of acetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$[3] and the dimethylation product, isobutyroyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)_2)$ (4)[4] (spectroscopic ratio after 36 h: 42:33:25).

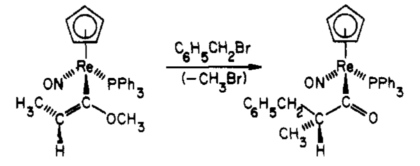


(1)

2 5 3

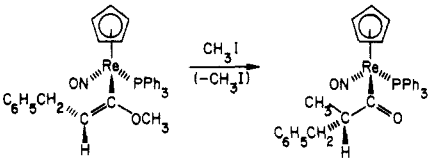
The conversion 2 → 3 is proposed to proceed via the methoxycarbene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_2CH_3)]^+I^-$ (5, eq 1). Indeed, when this reaction is monitored by ^1H NMR in CD_2Cl_2, an intermediate with plausible resonances for 5 is observed (δ (−35 °C, two isomers)[3] 5.71, 6.01 (s, C_5H_5), 3.70, 4.15 (s, OCH_3), 0.79, 1.11 (t, CCH_3)). Subsequently, iodide ion effects O-demethylation, analogously to previous observations with cationic iron methoxycarbene complexes.[5] The acyl byproducts which accompany 3 likely arise via proton transfer from 5 to 2. Indeed, the deprotonation product of 5, 6 (see below), is also observed by ^1H NMR during the course of eq 1. Malisch has reported similar side reactions in alkylations of iron α-methoxyvinyl complexes.[6]

Having established the ready nucleophilicity of α-methoxyvinyl complexes, we next examined their effectiveness in 1,3-asymmetric induction reactions. The substrates (Z)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHCH_3)$ (6, eq 2)[4] and (Z)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHCH_2C_6H_5)$ (7, eq 3)[4] were isolated in 72% and 81% overall yields by reactions of the corresponding acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2R)$ with first $(CH_3)_3O^+PF_6^-$ (CH_2Cl_2, 25 °C) to give methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_2R)]^+PF_6^-$ and then the base DBU.[7] By all spectroscopic criteria, 6 and 7 were isomerically pure. Both exhibited a 33 ± 5% ^1H NOE enhancement[8] of the vinyl hydrogen resonance upon irradiation of the α-methoxy resonance, as would be expected of Z geometric isomers.[2a] The structure of 7 was verified by X-ray crystallography.[9]



(2)

6 (SR,RS)-8



(3)

7 (SS,RR)-8

Complex 6 was treated with $C_6H_5CH_2Br$ (CH_2Cl_2; 25 °C, 12 h, and then 50 °C, 2 h). Acyl complex (SR,RS)-$(\eta^5\text{-}$

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[2] (a) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745. (b) Curtis, P. J.; Davies, S. G. *Ibid.* **1984**, 747.

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

[4] Microanalytical, IR, and NMR (^1H, ^{13}C, ^{31}P) data for each new compound are given in the supplementary material. In compounds with two chiral centers, the absolute configuration at rhenium is specified first.

[5] (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Cutler, A. R. *Ibid.* **1979**, *101*, 604.

[6] Grotsch, G.; Malisch, W. *J. Organomet. Chem.* **1983**, *246*, C42, C49.

[7] When the reactions of 6, 7, and related complexes with DBU and other bases were monitored by ^{31}P NMR at −78 °C, transients believed to be E geometric isomers were observed (E/Z as high as 88:12). These isomerized (in a process that was inhibited by added NaH) to Z isomers upon warming. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

[8] Noggle, J. H.; Shirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.

[9] The X-ray crystal structure of 7 will be described in a separate publication.

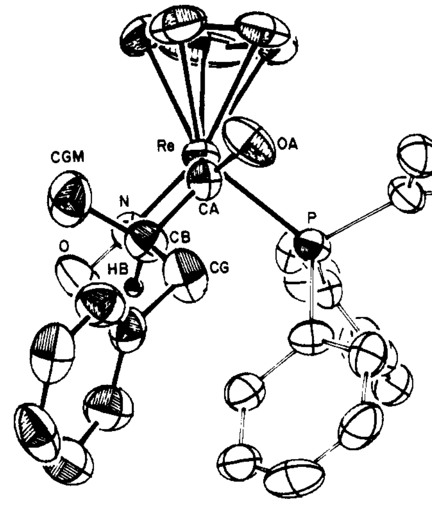
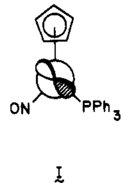


Figure 1. Molecular structure of (*SR,RS*)-(η^5-C_5H_5)Re(NO)-(PPh_3)(COCH(CH_3)$CH_2C_6H_5$)·$(THF)_{0.5}$. Important bond lengths (Å) and angles (deg): Re–C(A), 2.081 (7); Re–P, 2.358 (3); Re–N, 1.758 (7); C(A)–O(A), 1.252 (10); C(A)–C(B), 1.531 (11); C(B)–C(GM), 1.452 (20); C(B)–C(G), 1.524 (11); N–O, 1.181 (9); N–Re–P, 93.4 (3); C(A)–Re–P, 88.3 (3); C(A)–Re–N, 95.6 (3); Re–C(A)–O(A), 122.7 (6); Re–C(A)–C(B), 121.4 (5); C(A)–C(B)–C(GM), 106.8 (9); C(A)–C(B)–C(G), 108.9 (7); Re–N–O, 177.0 (6). The hydrogen is assigned an arbitrary radius.

C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)$CH_2C_6H_5$) ((*SR,RS*)-**8**)[4] was subsequently isolated in 71% yield (eq 2). The stereochemistry of a 0.5 THF solvate of (*SR,RS*)-**8** was established by X-ray crystallography as described in the supplementary material. Complex **7** was similarly treated with CH_3I (CH_2Cl_2; 25 °C, 12 h, and then 50 °C, 2 h). The opposite acyl complex diastereomer (*SS,RR*)-**8**[4] was subsequently isolated in 88% yield (eq 3). Diastereomers (*SR,RS*)-**8** and (*SS,RR*)-**8** showed no tendency to interconvert under the workup conditions employed. HPLC analyses of the reaction mixtures from eq 2 and 3 prior to workup indicated diastereomer ratios of (99 ± 1):(1 ± 1). Hence, efficient 1,3-asymmetric induction occurred.

The molecular structure of (*SR,RS*)-**8**, and important bond lengths and angles, are given in Figure 1. The torsion angle between the planes defined by N–Re–CA and Re–CA–OA is 0.5°, indicating an almost perfectly antiperiplanar relationship of the NO ligand to the acyl C=O moiety. In this conformation, overlap of C=O π^* acceptor orbital with the rhenium d orbital HOMO (shown in I)[10] is maximized. Together with our earlier X-ray crystal structure of (η^5-C_5H_5)Re(NO)(PPh_3)(CHO),[11] this study provides the second[12] direct structural comparison of homologous acyl and formyl complexes.

The configuration of the asymmetric carbon in (*SR,RS*)-**8** is that which would be expected if eq 2 proceeded



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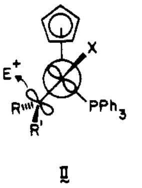

II

via transition state II—our previously proposed model for electrophilic attack upon (η^5-C_5H_5)Re(NO)(PPh_3)(C(X)=CRR′) complexes.[1] In this transition state, the Re–C_α conformation is such that overlap of the C=C π^* acceptor orbital with I is maximized. This should, by analogy to enamine C-alkylation reactions,[13] maximize the nucleophilicity of C_β. The electrophile then attacks C_β opposite the bulky PPh_3 ligand.[14]

In summary, we have shown that chiral (α-methoxyvinyl)rhenium complexes undergo facile C_β electrophilic attack with highly efficient 1,3-asymmetric induction. In addition, we have defined the stereochemistry of these transformations. The development of other highly stereoselective carbon–carbon bond forming reactions involving these complexes is in progress.

Acknowledgment. We thank the NIH for support of this research and Dr. J. P. Hutchinson for assistance with the X-ray crystal structure determination.

Supplementary Material Available: Characterization of new compounds and crystallographic data (43 pages).[4] Ordering information is given on any current masthead page.

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[13] Bláha, K.; Gerinka, D. *Adv. Heterocycl. Chem.* **1966**, *6*, 147.

[14] There is a second Re–C_α conformation (besides the one in II) in which overlap of I with the C=C π^* acceptor orbital is maximized. Data from our previous study[1] indicate this to be a far less reactive Re–C_α conformer than the one in II. Note that the two conformers give different Re^+=C geometric isomers upon electrophilic attack.

An NOE Difference NMR Study of a Conformationally Labile Organometallic Compound

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Summary: An NOE difference NMR study of the compound CpFe(CO)(PPh_3)CH_2SiMe_3 suggests that the (trimethylsilyl)methyl group preferentially oscillates between the cyclopentadienyl and triphenylphosphine ligands.

There is currently considerable interest in stereospecific and stoichiometric reactions of organotransition-metal compounds, especially with respect to reactions of metal–carbon σ-bonds[1] and the utilization of chiral organometallic compounds to effect stoichiometric[2] and catalytic[3] organic syntheses. While various attempts have been made to rationalize the stereochemical consequences of specific reactions on the basis of steric and/or electronic factors,[4,5] however, progress in this area is at present seriously hampered by lack of knowledge of the conformational properties in solution of many types of flexible organometallic compounds.

An attempt to deal with the problem of conformational preferences of coordinated alkyl groups of a series of compounds was reported by us in the early 1970s.[6] For

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[2] Davies, S. G. "Organotransition Metal Chemistry: Application to Organic Synthesis"; Pergamon Press: Oxford, 1982.

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[5] 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.