Synthesis and Reactivity of Chiral Rhenium Indenyl Complexes of the Formula $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(X)]^{n+}$

Yuanlin Zhou, Michael A. Dewey, and J. A. Gladysz*

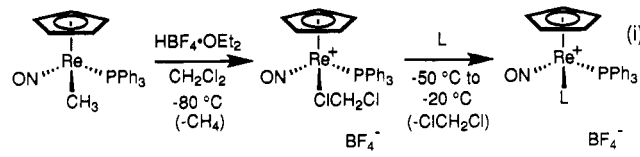
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 26, 1993®

Reaction of $(\eta^5\text{-}C_9H_7)Re(CO)_3$ and $NO^+BF_4^-$ yields $[(\eta^5\text{-}C_9H_7)Re(NO)(CO)_2]^+BF_4^-$ (**2**, 94%), which with PPh_3 ($ClCH_2CH_2Cl$, reflux) gives $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**3**, 94%). When **2** is dissolved in acetone, addition products of the formula $(\eta^1\text{-}C_9H_7)Re(NO)(CO)_2(\eta^1\text{-}O{=}C(CH_3)_2)_2$ form. Attempted reduction of the CO ligand in **3** yields hydride complexes. However, reaction of **2** and $NaBH_4$ gives $(\eta^5\text{-}C_9H_7)Re(NO)(CO)(CH_3)$ (**6**, 45%), which with PPh_3 ($ClCH_2CH_2Cl$, reflux) yields $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_3)$ (**5**, 18%) and $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(COCH_3)$ (**7**, 54%). Reaction of **5** and $HBF_4{\cdot}OEt_2$ in CH_2Cl_2 at −80 °C gives the unstable, substitution-labile dichloromethane complex $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**8**), which is characterized by NMR. Subsequent addition of acetone or cyclohexanone yields σ-ketone complexes $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}CR_2)]^+BF_4^-$ (82–76%), and addition of CO (250 psi) gives **3** (92%). In another approach to **5** and **8**, **3** and $NaOCH_3$ are combined to give $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO_2CH_3)$ (**11**, 92%). Sequential reactions with CH_3MgBr and $BH_3{\cdot}THF$ produce **7** (53%) and $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_2CH_3)$ (**12**, 95%). The latter could not be converted to **8** in high yield. However, reaction of **12** and HI affords $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(I)$ (88%), which with $CuCH_3$ gives **5** (62%).

Soon after the first transition metal complexes containing η^5-cyclopentadienyl ligands ($\eta^5\text{-}C_5H_5$) were synthesized, Fischer reported the η^5-indenyl analogs $(\eta^5\text{-}C_9H_7)_2Co$ and $(\eta^5\text{-}C_9H_7)_2Fe$.[1] Although indenyl complexes now have an extensively developed descriptive chemistry, they have figured more prominently in mechanistic organometallic chemistry. This originates from Mawby's 1969 report of enhanced reactivity of indenyl vs cyclopentadienyl molybdenum methyl tricarbonyl complexes in PX_3-induced CO insertions.[2] These transformations were proposed to involve η^5 to η^3 linkage isomerizations or "slippage" of the C_xH_y ligands—a process that in the indenyl case would be assisted by restoration of full aromaticity to the fused benzenoid ring. Subsequent studies of substitution reactions, which established enormous 10^8 rate accelerations for certain rhodium complexes, led Basolo to propose the term *kinetic indenyl ligand effect* for this general phenomenon.[3-7]

Over the past 8 years, we have conducted an extensive study of the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$.[8] This species is easily generated from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ in either racemic or enantiomerically pure form, as sketched in eq i. It decomposes above −20



°C, and isolation attempts have not been successful. However, it readily reacts with weak neutral donor ligands such as ketones, alkenes, and primary alkyl iodides to give Lewis base adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ in high yields.[8,9] In all cases, substitution occurs with retention of configuration at rhenium and very high enantioselectivity. Thus, the dichloromethane complex serves as a functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**). A related chlorobenzene complex behaves similarly.[10]

As further analyzed in the following paper,[11] certain aspects of the preceding substitution processes are arcane—particularly the origin of the high stereochemical fidelity. Hence, we sought to clarify the nature of the reaction coordinate. The possibility of cyclopentadienyl ligand slippage was consistent with preliminary rate data and precedented in reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$ described by Casey.[12] Thus, we set out to prepare indenyl analogs for mechanistic experiments. In this

® Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) (a) Fischer, E. O.; Seus, D.; Jira, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1953**, *8B*, 692. (b) Fischer, E. O.; Seus, D. *Ibid.* **1953**, *8B*, 694.

(2) (a) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403. (b) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (c) Hart-Davis, A. J.; White, C.; Mawby, R. J. *Ibid.* **1970**, *4*, 441. (d) Jones, D. J.; Mawby, R. J. *Ibid.* **1972**, *6*, 157.

(3) (a) Rerek, M. E.; Ji, L. N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740. (c) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (d) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198–200*, 219.

(4) Bang, H.; Lynch, T. J.; Basolo, F. *Organometallics* **1992**, *11*, 40.

(5) Basolo, F. *Polyhedron* **1990**, *9*, 1503.

(6) Casey, C. P.; O'Connor, J. M. *Chem. Rev.* **1987**, *87*, 307.

(7) For recent examples of enhanced reactivity of indenyl complexes in other than substitution reactions, see (a) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357 and references therein. (b) Foo, T.; Bergman, R. G. *Ibid.* **1992**, *11*, 1811. (c) Monti, D.; Bassetti, M. *J. Am. Chem. Soc.* **1993**, *115*, 4658.

(8) (a) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672. (b) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (c) Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33.

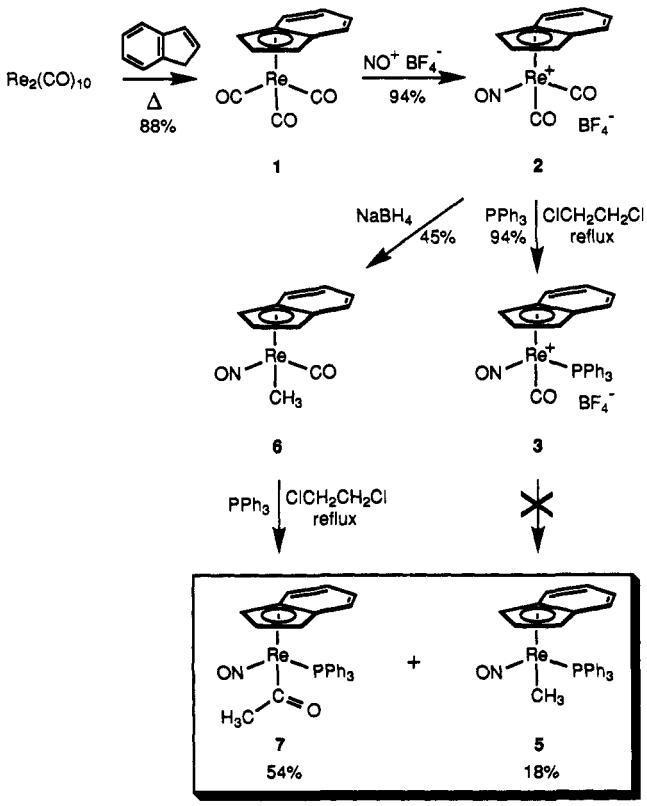
(9) Some lead references: (a) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. (b) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1990**, *112*, 9198. (c) Dalton, D. M.; Gladysz, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2741. (d) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699.

(10) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(11) Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A. *Organometallics*, following paper in this issue.

0276-7333/93/2312-3918$04.00/0

Scheme I. Syntheses of Rhenium Indenyl Carbonyl and Methyl Complexes



paper, we report the synthesis and characterization of a variety of neutral and cationic rhenium indenyl complexes of formula $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(X)]^{n+}$. Companion rate studies are detailed in the following paper.[11]

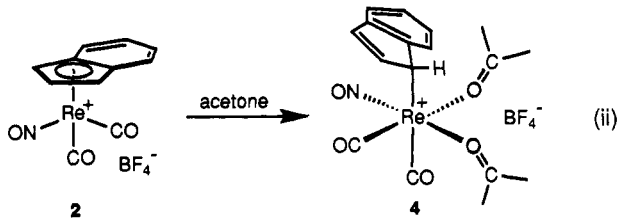
Results

1. Syntheses of Indenyl Carbonyl Complexes. The cyclopentadienyl methyl complex employed as the starting material in eq i was prepared by $NaBH_4$ reduction of the cationic monocarbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$.[13,14] This compound was in turn accessed from the tri- and dicarbonyl complexes $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$. Thus, we first sought to synthesize the corresponding series of indenyl carbonyl compounds.

The indenyl tricarbonyl complex $(\eta^5\text{-}C_9H_7)Re(CO)_3$ (**1**) proved to be a known compound.[15,16] It has been prepared, among other methods,[15] by the direct reaction of $Re_2(CO)_{10}$ and indene (Scheme I).[16] We isolated **1** in 88% yield by this route, as detailed in the Experimental Section. Reaction of **1** and $NO^+BF_4^-$ then gave the dicarbonyl nitrosyl complex $[(\eta^5\text{-}C_9H_7)Re(NO)(CO)_2]^+BF_4^-$ (**2**)—to the best of our knowledge a new compound—in 94% yield. The manganese analog has been similarly obtained utilizing $NO_2^+BF_4^-$.[17] Complex **2**, and all isolable compounds below, were characterized by microanalysis and IR and NMR spectroscopy (Experimental Section).

Interestingly, a synthesis of the target monocarbonyl complex $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**3**) from the dicarbonyl phosphine complex $(\eta^5\text{-}C_9H_7)Re(PPh_3)(CO)_2$ and $NO_2^+BF_4^-$ was reported in 1981.[17] However, the yield was very low (7%), and only IR data were given. Thus, we sought to oxidatively remove one of the carbonyl ligands in **2** with iodosobenzene in a donor solvent, as previously described for the cyclopentadienyl analog.[13,14] Subsequent addition of PPh_3 would then be expected to give **3**.

However, the dissolution of **2** in acetone or acetonitrile appeared to give η^1-indenyl complexes, as exemplified in eq ii. Thus, the reaction of **2** and acetone-d_6 was monitored



(one of several isomers)

by ^1H NMR at ambient temperature. Two major peaks appeared with chemical shifts characteristic of η^1-indenyl ReCH protons (δ 3.58, 3.49).[12b] Two minor peaks were also present (<10% total). The sample was kept at 57 °C for 0.5 h. A ^1H NMR spectrum (room temperature) showed >95% conversion to the species with the δ 3.58 resonance. The ^{13}C NMR spectrum exhibited two C=O and C≡O resonances (ppm: 235.1, 234.3; 187.3, 186.7). Hence, the product was assigned as the bis(acetone) complex $[(\eta^1\text{-}C_9H_7)Re(NO)(CO)_2(\eta^1\text{-}O{=}C(CD_3)_2)_2]^+BF_4^-$ (**4**-d_{12}).[18] Hexane was added in an attempt to precipitate **4**-d_{12}. However, the material isolated lacked η^1- or η^5-indenyl ^1H NMR resonances.

Acetonitrile-d_3 solutions of **2** also gave ^1H NMR signals in the η^1-indenyl region. Efforts to subsequently effect conversion to the phosphine complex **3** were unsuccessful. Hence, **2** and PPh_3 were refluxed in the poorly coordinating solvent $ClCH_2CH_2Cl$ (Scheme I). After 1 h, workup gave **3** in 94% yield. Interestingly, earlier attempts to effect analogous thermal substitutions with the cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ were unsuccessful.[13] As a check, this compound and PPh_3 were similarly refluxed in $ClCH_2CH_2Cl$. After 2 h, workup gave a sample that had been 55% converted to the phosphine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$. A 5-h reaction gave 90% conversion. At longer times, complete conversion was observed, and an optimized procedure is given in the Experimental Section. However, unlike **2**, the reactant is only sparingly soluble in $ClCH_2CH_2Cl$. Thus, the difference in preparative substitution rates does not establish a kinetic indenyl ligand effect.

2. Syntheses of Indenyl Methyl and Dichloromethane Complexes. In a procedure analgous to that utilized in the cyclopentadienyl series, the monocarbonyl

(12) (a) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535. (b) Casey, C. P.; O'Connor, J. M. *Ibid.* **1985**, *4*, 384. (c) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.

(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.

(14) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211.

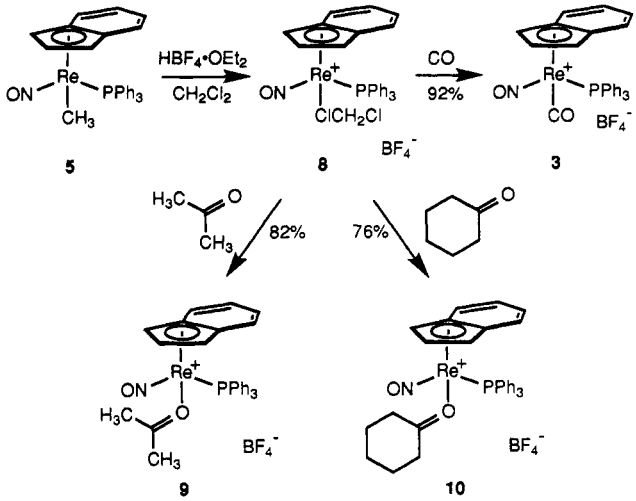
(15) Fischer, E. O.; Fellmann, W. *J. Organomet. Chem.* **1963**, *1*, 191.

(16) (a) Zdanovich, V. I.; Lobanova, I. A.; Kolobova, N. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 2149. (b) Miguel, D.; Steffan, U.; Stone, F. G. A. *Polyhedron* **1988**, *7*, 443.

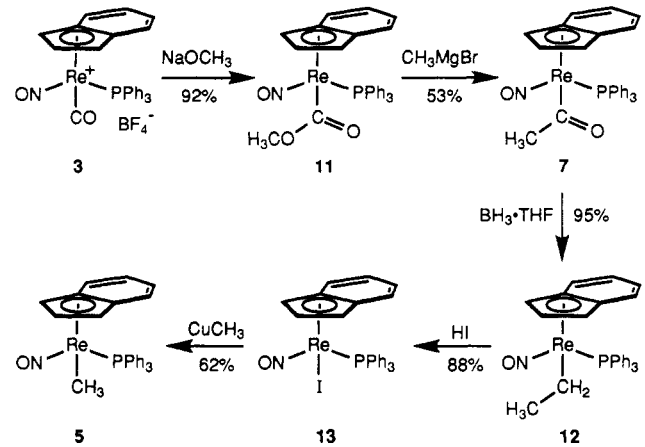
(17) Kolobova, N. E.; Lobanova, I. A.; Zdanovich, V. I.; Petrovskii, P. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 935.

(18) The isomer of **4**-d_n in which the carbonyl ligands, the acetone ligands, and the unique ligands (η^1-indenyl, nitrosyl) are mutually *trans* should give only one C=O and one C≡O ^{13}C NMR resonance and can be excluded. Casey finds that rhenium η^1-indenyl tricarbonyl complexes of the formula $(\eta^1\text{-}C_9H_7)Re(CO)_3(PR_3)_2$ exist exclusively as facial isomers.[12b] We believe it likely that the three best π accepting ligands in **4**-d_n (CO, CO, NO) also prefer a facial geometry.

Scheme II. Generation and Reactions of the Rhenium Indenyl Dichloromethane Complex 8



Scheme III. Other Routes to and Reactions Involving the Rhenium Indenyl Acetyl Complex 7



phosphine complex **3** was treated with 5 equiv of $NaBH_4$ in THF. However, only ca. 20% of the desired phosphine methyl complex $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_3)$ (**5**) formed, as assayed by ^1H NMR and IR. Rather, two rhenium hydride products dominated, as evidenced by ^1H NMR signals (δ, $CDCl_3$) at −8.39 (s) and −9.95 (d, J_{HP} 32.0 Hz). These were provisionally attributed to $(\eta^5\text{-}C_9H_7)Re(NO)(CO)(H)$ and $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(H)$ (ca. 50% and 30%), respectively. Other hydride reductants did not give improved yields of **5**.

Hence, an alternative route to **5** was investigated. First, the dicarbonyl complex **2** was treated with $NaBH_4$ in THF (Scheme I). Workup gave the carbonyl methyl complex $(\eta^5\text{-}C_9H_7)Re(NO)(CO)(CH_3)$ (**6**) in 45% yield. A ^1H NMR spectrum of the crude reaction mixture showed only traces of rhenium hydride products. Reaction of **6** and PPh_3 in refluxing $ClCH_2CH_2Cl$ then gave the phosphine methyl complex **5** and the phosphine acetyl complex $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(COCH_3)$ (**7**) in 18% and 54% yields after workup. Although the yield of **5** was poor, sufficient quantities could be produced for the rate study in the following paper.[11] Another synthesis of **5** is given below.

Next, **5** and $HBF_4\cdot OEt_2$ were combined at −80 °C in CH_2Cl_2 under conditions analgous to those in eq i, and $^{31}P\{^1H\}$ NMR spectra were recorded at −70 °C (Scheme II). Within 5 min, the indenyl dichloromethane complex $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**8**) had formed in high spectroscopic yield (12.6 ppm). Some very minor byproducts, which gave resonances barely above the baseline, were also apparent. A $^{13}C\{^1H\}$ NMR spectrum showed a doublet for the $ClCH_2Cl$ carbon at 74.2 ppm ($^3J_{CP}$ 2.6 Hz). The corresponding cyclopentadienyl complex exhibits ^{31}P and ^{13}C NMR resonances at 12.5 and 78.3 (d, $^3J_{CP}$ 3.7 Hz) ppm, respectively.[8b]

Similar reactions were conducted in CD_2Cl_2. These gave the deuteriodichloromethane complex **8**-d_2, which was characterized by ^1H NMR. Only one set of indenyl resonances was observed ($\eta^5\text{-}C_5H_3$ at δ 6.38 (br d), 5.63 (br s), 5.27 (br s)). Solutions of **8**-d_n showed little decomposition on the time scale of 1 h between −30 and −20 °C. However, extensive decomposition occurred over the course of 1 h at −10 °C, as reflected by a multitude of ^{31}P NMR signals between 12–14 and 19–21 ppm.

Complex **8** cleanly reacted with most donor ligands investigated (Scheme II). For example, acetone and cyclohexanone (6–10 equiv) gave the σ-ketone complexes $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+BF_4^-$ (**9**) and $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_2)_4CH_2)]^+BF_4^-$ (**10**) in 82% and 76% yields after workup. The spectroscopic properties of these compounds (Experimental Section) closely matched those of the cyclopentadienyl analogs.[9b,c] Acetone solutions of **9** showed no decomposition or conversion to η^1-indenyl addition products over the course of 3 h at room temperature. The reaction of **8** and carbon monoxide (250 psi) gave the carbonyl complex **3** in 92% yield after workup.

The reactions of **8** with acetone and cyclohexanone were monitored by $^{31}P\{^1H\}$ NMR. Complex **9** slowly formed at −60 °C. The probe was warmed to 0 °C over the course of 40 min. After 15 min at 0 °C, only **9** was present (18.9 ppm). Similarly, **10** slowly formed at −70 °C. The probe was warmed to −20 °C over the course of 30 min. After 15 min at −20 °C, only **10** was present (19.5 ppm). In contrast, **8** and the more nucleophilic ketone tropone (2 equiv) reacted at −80 °C to give four major products with ^{31}P NMR signals between 19.1 and 26.4 ppm. Larger excesses of tropone also gave several products. When samples were warmed, the product distributions did not improve.

3. Additional Chemistry of the Indenyl Acetyl Complex. In an attempt to develop more efficient routes to the dichloromethane complex **8**, an alternative synthesis and further chemistry of the acetyl complex **7** was investigated. First, the cationic carbonyl complex **3** and $NaOCH_3$ were combined (Scheme III). Addition occurred to give the methoxycarbonyl or "methyl ester" complex $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO_2CH_3)$ (**11**) in 92% yield after workup. Subsequent reaction with CH_3MgBr replaced the methoxy group, affording the acetyl complex **7** in 53% yield. Reduction of **7** with $BH_3\cdot THF$ then gave the ethyl complex $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_2CH_3)$ (**12**) in 95% yield. Analogous transformations have previously been effected in the cyclopentadienyl series.[13,14,19]

Next, **12** and $HBF_4\cdot OEt_2$ were combined in CH_2Cl_2 at −80 °C. A $^{31}P\{^1H\}$ NMR spectrum (−60 °C) showed the formation of a 10:68:22 mixture of two new compounds and **8** (19.7 (br), 13.8, 12.5 ppm). A ^1H NMR spectrum suggested that the major product was the ethyl hydride complex $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_2CH_3)(H)]^+BF_4^-$, as evidenced by a doublet at δ −3.29 ($^2J_{HP}$ 67.3 Hz). The related benzyl hydride complex $[(\eta^5\text{-}C_5H_5)Re(NO)$-

(19) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

$(PPh_3)(CH_2C_6H_5)(H)]^+BF_4^-$ was found to exhibit a ^1H resonance at δ −3.72 ($^2J_{HP}$ 65.7 Hz).[8b] Excess acetone was added, and the sample was warmed to room temperature. A $^{31}P\{^1H\}$ NMR spectrum showed the formation of many products. Hence, this three-component mixture does not serve as a functional equivalent of the indenyl rhenium Lewis acid $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)]^+$. A second sample was warmed in the absence of acetone. All species showed extensive decomposition on the time scale of 1.2 h at −20 °C.

Other strategies, precedented in the cyclopentadienyl series, for the conversion of **12** to **8** were then pursued.[20,21] First, reaction of **12** and aqueous HI gave the iodide complex $(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(I)$ (**13**) in 88% yield after workup. Subsequent addition of $CuCH_3$ displaced the iodide ligand, giving the methyl complex **5** in 62% yield. Thus, the acetyl complex byproduct **7** produced in Scheme I can be converted in three steps to the corresponding methyl complex **5** and then to the dichloromethane complex **8**.

Discussion

The preparative data summarized in Schemes I-III establish that indenyl analogs of many previously reported cyclopentadienylrhenium complexes can be accessed. However, in some cases significant procedural modifications are required. In particular, there appears to be a richer metal-centered chemistry, as witnessed by (1) the conversion of η^5-indenyl complex **2** to η^1-indenyl complex **4** (eq ii), (2) the displacement of carbonyl and PPh_3 ligands in **3** by hydride reagents, as opposed to carbonyl ligand reduction, and (3) the multitude of products obtained from **8** and tropone. These trends are logically attributed to the greater ease of C_xH_y ligand slippage in indenyl complexes.

Reactions of the indenyl tricarbonyl complex **1** with phosphines and phosphites have been previously studied by Casey,[12b] Lynch, and Basolo.[4] In the case of PMe_3 and $P(n\text{-}Bu)_3$, addition occurs to give the η^1 complexes $(\eta^1\text{-}C_9H_7)Re(CO)_3(PR_3)_2$. However, other phosphines and phosphites, including bulky PCy_3 (Cy = cyclohexyl), give mixtures of η^1 addition products and the η^5 substitution products $(\eta^5\text{-}C_9H_7)Re(CO)_2(PX_3)$. Thus, the partitioning between η^1 and η^5 complexes can be a sensitive function of nucleophile. Also, under appropriate conditions many of the η^1 addition products can be transformed to η^5 substitution products.

Similar contrasts are apparent in our chemistry. For example, the dicarbonyl complex **2** and acetone solvent react to give an addition product, η^1-indenyl bis(acetone) complex **4** (eq ii). However, the dichloromethane complex **8** and excess acetone react without detectable intermediates to give a substitution product, η^5-indenyl acetone complex **9**—which is stable in acetone solvent. Also, $NaBH_4$ reduces the dicarbonyl complex **2** to the carbonyl methyl complex **6**. However, under identical conditions the carbonyl phosphine complex **3** gives mainly hydride complexes.

Although Schemes I-III adequately meet the preparative needs of this and the following paper, several issues deserve emphasis. First, there is room for improvement of many of the yields. Second, the corresponding cyclopentadienyl and pentamethylcyclopentadienyl complexes can be resolved into enantiomers via (1-naphthyl)ethylamine adducts of the formula $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(CONHCH(CH_3)C_{10}H_7)$.[14,22] However, attempts to generate an analogous complex from **3** or **11** gave numerous products, as assayed by $^{31}P\{^1H\}$ NMR. Thus, routes to enantiomerically pure indenyl rhenium complexes remain to be developed. Indeed, to our knowledge no chiral-at-metal η^5-indenyl complexes are presently available in nonracemic form. It would obviously be of interest to determine the stereochemistry of substitution of the dichloromethane complex **8** and whether a reaction sequence involving $\eta^5 \rightarrow \eta^1 \rightarrow \eta^5$-indenyl complexes can proceed without racemization.

The ^1H and ^{13}C NMR properties of η^5-indenyl ligands have been previously analyzed in detail.[23] We assigned the ^{13}C resonances in our complexes (Experimental Section) on the basis of chemical shift trends established earlier.[24] In many cases, the ^1H resonances of the $\eta^5\text{-}C_5H_3$ grouping show similar shielding patterns.[23b,c,f] However, we did not assign individual indenyl ^1H NMR resonances for most compounds, as first-order coupling behavior was usually not observed.

The IR ν_{CO} values of the σ-ketone complexes **9** and **10** (1618–1620 cm^{-1}) are essentially identical with those of the cyclopentadienyl analogs (1619–1622 cm^{-1}).[9b,c] Also, the IR ν_{NO} of **9** and **10** are within 6 cm^{-1} of those of the cyclopentadienyl complexes, and the ^{31}P NMR chemical shifts differ by ≤1 ppm. Similar correspondence is observed for the other indenyl complexes when spectral data are acquired in identical media. Much greater differences are found with pentamethylcyclopentadienyl derivatives. Thus, the indenyl ligand appears to only slightly perturb the electronic properties of the rhenium fragment.

In summary, a number of chiral rhenium indenyl complexes of the formula $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(X)]^{n+}$ are now readily available. These will be the subject of future mechanistic studies, as exemplified in the following paper.

Experimental Section[25]

$(\eta^5\text{-}C_9H_7)Re(CO)_3$ (1). A Schlenk flask was charged with $Re_2(CO)_{10}$ (12.00 g, 18.39 mmol), indene (35 mL), and a stir bar and was fitted with a condenser. The mixture was stirred under

(20) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(21) Ramsden, J. A.; Peng, T.-S.; Gladysz, J. A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 625.

(22) Huang, Y.-H.; Niedercorn, F.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *383*, 213.

(23) (a) Köhler, F. H. *Chem. Ber.* **1974**, *107*, 570. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (c) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329. (d) Johnston, P.; Loonat, M. S.; Ingham, W. L.; Carlton, L.; Coville, N. J. *Organometallics* **1987**, *6*, 2121. (e) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777. (f) Ceccon, A.; Elsevier, C. J.; Ernsting, J. M.; Gambaro, A.; Santi, S.; Venzo, A. *Inorg. Chim. Acta* **1993**, *204*, 15.

(24) The CH ^{13}C resonances of the five membered ring (C-1,2,3) are upfield of those of the six membered ring (C-4,5,6,7). Also, C-1,3 are upfield of C-2, and C-5,6 are upfield of C-4,7. The carbons that lack hydrogens (C-3a,7a) give resonances of reduced intensity.[23]

(25) Reactions were carried out under dry N_2 atmospheres. NMR and IR spectra were recorded on Varian XL-300 and Mattson Polaris FT spectrometers. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in open capillaries and were corrected. Solvents were treated as follows: CH_2Cl_2 and CH_3OH, distilled from CaH_2; ether and THF, distilled from Na/benzophenone; hexane, toluene, and benzene, distilled from Na; acetone, distilled from K_2CO_3; $CDCl_3$ and CD_2Cl_2, vacuum transferred from CaH_2; $ClCH_2CH_2Cl$ and acetone-d_6, used as received. The reagents $NO^+BF_4^-$, $NaBH_4$, PPh_3, $NaOCH_3$ (4.37 M in CH_3OH), $CuBr\cdot S(CH_3)_2$, CH_3MgBr, and BH_3-THF were used as received from Aldrich. Indene (90%, Aldrich) was distilled and passed through silica gel, $Re_2(CO)_{10}$ (Pressure Chemicals) and CO (Matheson) were used as received, $HBF_4\cdot OEt_2$ (Aldrich) was standardized as described previously,[8b] and HI (57%, Aldrich) was distilled.

vacuum, saturated with N_2, and placed in a ca. 220 °C oil bath. After 12 h of reflux, excess indene was removed by distillation. Hexane (40 mL) was added to the residue with stirring, and the mixture was stored in a freezer overnight. The solid was collected by filtration, washed with cold hexane (10 mL), and dried under oil pump vacuum to give **1** (12.47 g, 32.36 mmol, 88%). The ^1H NMR and IR spectra were identical with those previously reported.[15,16]

$[(\eta^5\text{-}C_9H_7)Re(NO)(CO)_2]^+BF_4^-$ (2). A Schlenk flask was charged with **1** (6.00 g, 15.6 mmol), CH_2Cl_2 (25 mL), and a stir bar, and was cooled to 0 °C. Then $NO^+BF_4^-$ (2.36 g, 20.2 mmol) was added with stirring (gas evolution). After 1 h at 0 °C, solvent was removed under oil pump vacuum. THF (15 mL) was added to the residue. The resulting yellow solid was collected by filtration, washed with THF (3 × 4 mL), and dried under oil pump vacuum to give **2** (6.92 g, 14.6 mmol, 94%), mp 129–131 °C. Anal. Calcd for $C_{11}H_7BF_4NO_3Re$: C, 27.86; H, 1.49; N, 2.95. Found: C, 27.77; H, 1.53; N, 3.00. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2108 (s), 2053 (s); ν_{NO} 1805 (vs).

NMR (CD_2Cl_2):[26] ^1H (δ) 7.85 (m, H-4,7 of C_9H_7), 7.57 (m, H-5,6 of C_9H_7), 6.73 (s, H-1,2,3 of C_9H_7); $^{13}C\{^1H\}$ (ppm) 182.3 (s, CO), C_9H_7 at[24] 133.8, 131.7 (2 s, C-4,7), 126.0, 123.7 (2 s, C-5,6), 99.6, 97.1 (2 s, C-3a,7a), 82.5 (s, C-2), 80.0 and 69.6 (2 s, C-1,3).

$[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (3). A Schlenk flask was charged with **2** (2.00 g, 4.22 mmol), PPh_3 (1.44 g, 5.48 mmol), $ClCH_2CH_2Cl$ (30 mL), and a stir bar and was fitted with a condenser. The solution was stirred under vacuum, saturated with N_2 and placed in a 90 °C oil bath. After 1 h of reflux, the solution was cooled to room temperature, concentrated to ca. 5 mL by rotary evaporation, and added dropwise to ether (100 mL). The resulting yellow precipitate was collected by filtration and dried under oil pump vacuum to give **3** (2.82 g, 3.98 mmol, 94%), mp 204–206 °C. Anal. Calcd for $C_{28}H_{22}BF_4NO_2PRe$: C, 47.47; H, 3.13. Found: C, 47.33; H, 3.21. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2021 (s); ν_{NO} 1765 (vs).

NMR (CD_2Cl_2):[26] ^1H (δ) 7.63–7.07 (m, 15H of $3C_6H_5$ and 4H of C_9H_7), 6.20 (t, J_{HH} 2.9, H-2 of C_9H_7), 6.04 (d, J_{HH} 2.9, H-1 of C_9H_7), 6.01 (d, J_{HH} 2.9, H-3 of C_9H_7); $^{13}C\{^1H\}$ (ppm) 194.3 (d, J_{CP} 7.8, CO), C_6H_5 at 133.3 (d, J_{CP} 11.9, *o*), 132.8 (s, *p*), and 129.9 (d, J_{CP} 11.4, *m*),[27] C_9H_7 at[24] 131.7, 131.6 (2 s, C-4,7), 125.0, 124.2 (2 s, C-5,6), 112.8, 112.0 (2 s, C-3a,7a), 98.4 (s, C-2), 80.9, and 80.8 (2 s, C-1,3); $^{31}P\{^1H\}$ (ppm) 12.6 (s).

$(\eta^1\text{-}C_9H_7)Re(NO)(CO)_2(\eta^1\text{-}O{=}C(CD_3)_2)_2$ (4-d_{12}). A 5-mm NMR tube was charged with **2** (0.0983 g, 0.207 mmol) and acetone-d_6 (0.65 mL) and was transferred to an ambient temperature NMR probe. Then ^1H and $^{13}C\{^1H\}$ NMR spectra were acquired as described in the text. The data that follow were obtained at ambient temperature after a 0.5-h period at 57 °C. IR (cm^{-1}, thin film): $\nu_{C=O}$ 2101 (s), 2028 (s); ν_{NO} 1783 (vs).[28]

NMR ($(CD_3)_2CO$):[26] ^1H (δ) 7.73 (dq, J_{HH} 7.4, 0.7, 1H of C_9H_7), 7.32 (d, J_{HH} 7.3, 1H of C_9H_7), 7.21 (tdd, J_{HH} 7.4, 1.1, 0.6, 1H of C_9H_7), 7.13 (td, J_{HH} 7.3, 1.1, 1H of C_9H_7), 6.85 (ddd, J_{HH} 5.7, 2.0, 0.6, 1H of C_9H_7), 6.53 (dd, 5.7, 2.0, 1H of C_9H_7), 3.58 (m, CHRe); $^{13}C\{^1H\}$ (ppm) 235.1 (s, $C_2C{=}O$), 234.3 (s, $C_2C{=}O$), 187.3 (s, CO), 186.7 (s, CO), C_9H_7 at[24] 146.1 (s), 146.0 (s), 137.9 (s), 132.7 (s), 127.2 (s), 126.0 (s), 125.2 (s), and 121.4 (s); 63.1 (s, CHRe).

$(\eta^5\text{-}C_9H_7)Re(NO)(CO)(CH_3)$ (6). A Schlenk flask was charged with **2** (2.00 g, 4.22 mmol), THF (60 mL), and a stir bar and was cooled to 0 °C. Then $NaBH_4$ (0.160 g, 4.22 mmol) was added with stirring. After 15 min at 0 °C, solvent was removed under oil pump vacuum, and the residue was extracted with benzene (15 mL). The extract was chromatographed on a silica gel column with benzene. Solvent was removed from the bright red eluate. The residue was dissolved in CH_2Cl_2 (5 mL), and hexane (30 mL) was added. The solution was concentrated to ca. 20 mL under oil pump vacuum and cooled in dry ice. After 2 h, the resulting red solid was collected by filtration and dried under oil pump vacuum to give **6** (0.710 g, 1.90 mmol, 45%), mp 61–61.5 °C. Anal. Calcd for $C_{11}H_{10}NO_2Re$: C, 35.29; H, 2.69; N, 3.74. Found: C, 35.74; H, 2.71; N, 3.73. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 1961 (s); ν_{NO} 1691 (vs).

NMR (CD_2Cl_2):[26] ^1H (δ) 7.50–7.15 (m, H-4,5,6,7 of C_9H_7), 6.04 (m, H-1,3 of C_9H_7), 5.60 (m, H-2 of C_9H_7), 0.26 (s, CH_3); $^{13}C\{^1H\}$ (ppm) 211.6 (s, CO), C_9H_7 at[24] 128.2, 127.0 (2 s, C-4,7), 124.3, 123.0, (2 s, C-5,6), 114.0, 110.1 (2 s, C-3a,7a), 92.3 (s, C-2), 78.5 and 74.7 (2 s, C-1,3); −27.1 (s, CH_3).

$(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(COCH_3)$ (7). A Schlenk flask was charged with **6** (0.680 g, 1.82 mmol), PPh_3 (1.10 g, 4.19 mmol), $ClCH_2CH_2Cl$ (60 mL), and a stir bar and was fitted with a condenser. The solution was stirred under vacuum, saturated with N_2, and placed in a 90 °C oil bath. After 15 min of reflux, solvent was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (2 mL), and hexane (20 mL) was added with stirring. The resulting yellow precipitate was collected by filtration and dried under oil pump vacuum to give **7** (0.620 g, 0.974 mmol, 54%), mp 200–203 °C dec. Anal. Calcd for $C_{29}H_{25}NO_2PRe$: C, 54.71; H, 3.96. Found: C, 54.45; H, 4.10. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1657 (vs); ν_{CO} 1559 (m).

NMR:[26] ^1H (δ, $CDCl_3$) 7.49–6.99 (m, 15H of $3C_6H_5$ and 2H of C_9H_7), 6.68 (t, J_{HH} 7.6, 1H of C_9H_7), 6.06 (m, 1H of C_9H_7), 5.98 (br s, 1H of C_9H_7), 5.85 (dd, J_{HH} 8.6, 1.1, 1H of C_9H_7), 4.42 (br d, J_{HH} 1.1, 1H of C_9H_7), 1.81 (s, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2) 195.5 (d, J_{CP} 12.5, CO), C_6H_5 at 133.6 (d, J_{CP} 11.2, *o*), 130.2 (s, *p*), and 128.0 (d, J_{CP} 10.8, *m*),[27] C_9H_7 at[24] 126.7, 125.9 (2 s, C-4,7), 124.4, 123.8 (2 s, C-5,6), 115.5, 108.6 (2 s, C-3a,7a), 99.2 (s, C-2), 79.8 and 78.7 (2 s, C-1,3); 49.8 (s, CH_3); $^{31}P\{^1H\}$ (ppm, $CDCl_3$) 15.2 (s).

$(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_3)$ (5). The supernatant that remained after the precipitation of **7** in the preceding experiment was chromatographed on a silica gel column with CH_2Cl_2/hexane (1:6 v/v; to remove PPh_3) and then CH_2Cl_2. Solvent was removed from the bright orange eluate under oil pump vacuum to give **5** as an orange powder (0.200 g, 0.329 mmol, 18%), mp 69–72 °C dec. Anal. Calcd for $C_{28}H_{25}NOPRe$: C, 55.25; H, 4.14; N, 2.30. Found: C, 55.35; H, 4.18; N, 2.25. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1630 (vs).

NMR:[26] ^1H (δ, CD_2Cl_2) 7.41–7.32 (m, 15H of $3C_6H_5$), 7.09–6.76 (m, H-4,5,6,7 of C_9H_7), 5.59 (t, J_{HH} 2.9, 1H of C_9H_7), 5.17 (m, 1H of C_9H_7), 4.68 (m, 1H of C_9H_7), 0.64 (d, J_{HP} 5.1, CH_3); $^{13}C\{^1H\}$ (ppm, $CDCl_3$) C_6H_5 at 135.1 (d, J_{CP} 51.9, *i*), 133.6 (d, J_{CP} 10.6, *o*), 129.9 (s, *p*), and 128.1 (d, J_{CP} 10.1, *m*), C_9H_7 at[24] 126.7, 125.5 (2 s, C-4,7), 124.8, 123.1 (2 s, C-5,6), 113.2, 110.5 (2 s, C-3a,7a), 90.7 (s, C-2), 76.5 and 74.8 (2 s, C-1,3); −28.2 (d, J_{CP} 6.1, CH_3); $^{31}P\{^1H\}$ (ppm, CD_2Cl_2) 25.9 (s).

$[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(ClCD_2Cl)]^+BF_4^-$ (8-d_2). A 5-mm NMR tube was charged with **5** (0.049 g, 0.081 mmol) and CD_2Cl_2 (ca. 0.5 mL) and was capped with a septum. The tube was cooled to −80 °C, $HBF_4{\cdot}OEt_2$ (0.0086 mL, 0.081 mmol) was added, and NMR spectra were recorded at −60 °C. ^1H NMR (δ): 7.75–6.73 (m, 15H of $3C_6H_5$ and 4H of C_9H_7), 6.38 (br d, J_{HH} 8.6, 1H of C_9H_7), 5.63 (br s, 1H of C_9H_7), 5.27 (br s, 1H of C_9H_7). $^{31}P\{^1H\}$ NMR (ppm): 12.6 (s). A sample of **8** was analogously generated in CH_2Cl_2. $^{13}C\{^1H\}$ NMR (ppm, −80 °C, unlocked): C_6H_5 at 132.3 (d, J_{CP} 9.2, *o*), 131.1 (s, *p*), 128.4 (d, J_{CP} 10.4, *m*);[27] C_9H_7 at[24] 130.4, 129.0 (2 s, C-4,7), 125.8, 123.7 (2 s, C-5,6), 115.8, 115.0 (2 s, C-3a, 7a), 91.2 (s, C-2), 76.1 and 71.3 (2 s, C-1,3); 74.2 (d, J_{CP} 2.6, CH_2).

$[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+BF_4^-$ (9). A Schlenk flask was charged with **5** (0.183 g, 0.300 mmol), CH_2Cl_2 (10 mL), and a stir bar and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.035 mL, 0.30 mmol) was added with stirring to generate **8**. Acetone (0.110 mL, 1.80 mmol) was added, and the cold bath was allowed to warm to room temperature over the course of several hours. The solution was concentrated to 2 mL under oil pump vacuum and added to ether (25 mL) via cannula. The resulting yellow precipitate was collected by filtration, washed with pentane (2 × 2 mL) and dried under oil pump vacuum to give **9** (0.182 g, 0.246 mmol, 82%), mp 115–117 °C dec. Anal. Calcd for $C_{30}H_{28}BF_4NO_2PRe$: C, 48.79; H, 3.82. Found: C, 48.05; H, 4.27. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1693 (vs); ν_{CO} 1620 (m).

(26) All coupling constants (*J*) are in Hz. Some of the smaller C_9H_7 ligand ^1H NMR couplings assigned as J_{HH} values may actually be J_{HP} values.

(27) The *ipso* carbon resonance was not observed.

(28) The IR spectrum was recorded immediately after depositing a thin film on a salt plate. However, an acetone ligand $\nu_{C=O}$ absorption (observed for **9**) was not detected.

NMR (CD_2Cl_2):[26] ^1H (δ) 7.56–7.08 (m, 15 H of $3C_6H_5$ and 2H of C_9H_7), 6.95 (m, 1H of C_9H_7), 6.79 (t, J_{HH} 7.6, 1H of C_9H_7), 6.66 (pseudo d, J_{HH} 8.5, 1H of C_9H_7), 5.74 (br d, J_{HH} 2.5, 1H of C_9H_7), 5.61 (br s, 1H of C_9H_7), 2.13 (d, J_{HP} 2.2, $2CH_3$); $^{13}C\{^1H\}$ (ppm) 230.3 (s, CO), C_6H_5 at 133.2 (d, J_{CP} 11.1, *o*), 131.6 (s, *p*), and 129.1 (d, J_{CP} 19.5, *m*),[27] C_9H_7 at[24] 129.3, 128.9 (2 s, C-4,7), 126.0, 123.3 (2 s, C-5,6), 118.1, 115.5 (2 s, C-3a,7a), 89.4 (s, C-2), 73.8 and 72.0 (2 s, C-1,3); 31.9 (s, $2CH_3$); $^{31}P\{^1H\}$ (ppm) 18.9 (s).

$[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{C(CH_2)_4CH_2}\,)]^+BF_4^-$ (10). Complex **5** (0.100 g, 0.164 mmol), CH_2Cl_2 (3 mL), $HBF_4{\cdot}OEt_2$ (0.018 mL, 0.16 mmol), and cyclohexanone (0.170 mL, 1.64 mmol) were combined in a procedure analogous to that given for **9**. A similar workup gave **10** (0.097 g, 0.125 mmol, 76%), mp 177–181 °C dec. Anal. Calcd for $C_{33}H_{32}BF_4NO_2PRe$: C, 50.91; H, 4.14. Found: C, 49.93; H, 4.16. A sample was dissolved in CH_2Cl_2 and layered with hexane. After 1 day, the resulting yellow needles were collected by filtration and dried under oil pump vacuum (0.5 h) to give **10**·CH_2Cl_2, mp 177–181 °C dec. Calcd for $C_{33}H_{32}BF_4NO_2PRe{\cdot}CH_2Cl_2$: C, 47.29; H, 3.97. Found: C, 47.39; H, 4.15. The presence of the monosolvate was verified by ^1H NMR (δ 5.30, 2H, $CDCl_3$). IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1693 (vs); ν_{CO} 1618 (m).

NMR (CD_2Cl_2):[26] ^1H (δ) 7.62–7.11 (m, 15 H of $3C_6H_5$ and 2H of C_9H_7), 7.09 (d, J_{HH} 7.2, 1H of C_9H_7), 6.87 (pseudo d, J_{HH} 8.6, 1H of C_9H_7), 6.15 (br s, 1H of C_9H_7), 5.91 (br s, 1H of C_9H_7), 5.13 (br s, 1H of C_9H_7), 2.34–1.49 (m, C_6H_{10}); $^{13}C\{^1H\}$ (ppm) 236.3 (s, CO), C_6H_5 at 133.8 (d, J_{CP} 10.8, *o*), 132.1 (s, *p*), 130.9 (d, J_{CP} 56.1, *i*), and 129.6 (d, J_{CP} 10.7, *m*), C_9H_7 at[24] 131.8, 130.1 (2 s, C-4,7), 127.4, 124.2 (2 s, C-5,6), 119.5, 113.5 (2 s, C-3a,7a), 90.0 (s, C-2), 76.3 and 73.9 (2 s, C-1,3); 42.5 (s, $2CH_2$), 27.6 (s, $2CH_2$), 23.8 (s, CH_2); $^{31}P\{^1H\}$ (ppm) 19.5 (s).

Preparation of 3 from 8. A Fischer–Porter bottle was charged with **5** (0.066 g, 0.108 mmol) and CH_2Cl_2 (10 mL), and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.0117 mL, 0.108 mmol) was added with shaking to generate **8**. Then CO was admitted (250 psi), and the cold bath was removed. After 7 h, the solution was concentrated under oil pump vacuum to ca. 1 mL and added dropwise to ether (15 mL). The resulting yellow solid was collected by filtration and dried under oil pump vacuum to give **3** (0.070 g, 0.099 mmol, 92%). The IR and $^1H/^{31}P$ NMR spectra were identical with those reported above.

$(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CO_2CH_3)$ (11). A Schlenk flask was charged with **3** (1.50 g, 2.12 mmol), CH_3OH (5 mL), and a stir bar. The suspension was stirred under vacuum and saturated with N_2. Then $NaOCH_3$ (1.70 mL, 4.37 M in methanol, 7.43 mmol) was added with stirring. After 40 min, the resulting yellow solid was collected by filtration, washed with CH_3OH (3 × 1 mL), H_2O (3 × 3 mL), and CH_3OH (2 × 1 mL) and dried under oil pump vacuum to give **11** (1.27 g, 1.95 mmol, 92%), mp 102–104 °C dec. Anal. Calcd for $C_{29}H_{25}NO_3PRe$: C, 53.37; H, 3.86. Found: C, 52.78; H, 3.84. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1674 (vs); ν_{CO} 1588 (m).

NMR ($CDCl_3$):[26] ^1H (δ) 7.54–7.00 (m, 15H of $3C_6H_5$ and 2H of C_9H_7), 6.74 (t, J_{HH} 7.8, 1H of C_9H_7), 6.30 (br s, 1H of C_9H_7), 6.03 (br s, 1H of C_9H_7), 5.78 (d, J_{HH} 8.2, 1H of C_9H_7), 4.34 (br s, 1H of C_9H_7), 3.02 (s, CH_3); $^{13}C\{^1H\}$ (ppm) 195.5 (d, J_{CP} 12.5, CO), C_6H_5 at 133.6 (d, J_{CP} 11.2, *o*), 130.2 (s, *p*), and 128.0 (d, J_{CP} 10.8, *m*),[27] C_9H_7 at[24] 126.7, 125.9 (2 s, C-4,7), 124.4, 123.8 (2 s, C-5,6), 115.5, 108.6 (2 s, C-3a,7a), 99.2 (s, C-2), 79.8 and 78.7 (2 s, C-1,3); 49.8 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 16.8 (s).

Preparation of 7 from 11. A Schlenk flask was charged with **11** (0.680 g, 1.04 mmol), toluene (30 mL), and a stir bar. Then CH_3MgBr (0.580 mL, 1.62 mmol, 2.80 M in ether) was added with stirring. After 20 min, solvent was removed under oil pump vacuum, and the residue was extracted with acetone (10 mL). The extract was filtered through silica gel, which was rinsed with acetone. Solvent was removed from the filtrate by rotary evaporation to give a yellow solid, which was washed with acetone (2 × 0.7 mL) and dried under oil pump vacuum to give **7** (0.350 g, 0.550 mmol, 53%). The IR and $^1H/^{31}P$ NMR spectra were identical with those reported above.

$(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(CH_2CH_3)$ (12). A Schlenk flask was charged with **7** (0.550 g, 0.864 mmol), THF (60 mL), and a stir bar. Then $BH_3{\cdot}THF$ (4.0 mL, 1M in THF, 4.0 mmol) was added with stirring. The solution was refluxed for 15 min, and solvent was removed under oil pump vacuum. The residue was chromatographed on a silica gel column with CH_2Cl_2. Solvent was removed from the orange eluate under oil pump vacuum to give **12** as an orange powder (0.512 g, 0.882 mmol, 95%), mp 146–150 °C dec. Anal. Calcd for $C_{29}H_{27}NOPRe$: C, 55.94; H, 4.37. Found: C, 56.64; H, 4.42. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1628 (vs).

NMR ($CDCl_3$):[26] ^1H (δ) 7.51–7.01 (m, 15H of $3C_6H_5$ and 2H of C_9H_7), 6.75 (m, 1H of C_9H_7), 6.43 (m, 1H of C_9H_7), 5.50 (t, J_{HH} 3.7, 1H of C_9H_7), 5.27 (m, 1H of C_9H_7), 4.63 (m, 1H of C_9H_7), 2.33 (m, CH_α), 1.40 (m, $CH_{\alpha'}$, CH_3); $^{13}C\{^1H\}$ (ppm) C_6H_5 at 133.6 (d, J_{CP} 10.4, *o*), 129.9 (s, *p*), and 128.0 (d, J_{CP} 10.0, *m*),[27] C_9H_7 at[24] 126.1, 125.8 (2 s, C-4,7), 124.2, 123.3 (2 s, C-5,6), 112.8, 111.4 (2 s, C-3a,7a), 93.8 (s, C-2), 76.1 and 74.9 (2 s, C-1,3); 24.0 (s, CH_3), −10.4 (d, J_{CP} 5.8, CH_2); $^{31}P\{^1H\}$ (ppm) 26.2 (s).

$(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(I)$ (13). A Schlenk flask was charged with **12** (0.350 g, 0.562 mmol), CH_2Cl_2 (7 mL), and a stir bar and was cooled to −40 °C. Aqueous HI (57%; 0.082 mL, 0.62 mmol) was added. The cold bath was allowed to warm to room temperature over the course of several hours. Solvent was removed under oil pump vacuum, and the residue was extracted with CH_2Cl_2 (2 mL). The extract was filtered through silica gel. Solvent was removed from the filtrate by rotary evaporation, and the red solid was dissolved in CH_2Cl_2 and layered with hexane. After 1 day, the resulting dark red prisms were collected by filtration and dried under oil pump vacuum to give **13** (0.355 g, 0.493 mmol, 88%), mp 191–193 °C dec. Anal. Calcd for $C_{27}H_{22}INOPRe$: C, 45.01; H, 3.08. Found: C, 44.76; H, 3.12. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1671 (vs).

NMR ($CDCl_3$):[26] ^1H (δ) 7.50–7.14 (m, 15H of C_6H_5 and 2H of C_9H_7), 6.93 (t of m, J_{HH} 7.6, 1H of C_9H_7), 6.44 (d of m, J_{HH} 8.5, 1H of C_9H_7), 6.10 (m, 1H of C_9H_7), 5.47 (td, J_{HH} 2.7, 1.0, 1H of C_9H_7), 4.82 (m, 1H of C_9H_7); $^{13}C\{^1H\}$ (ppm) C_6H_5 at 134.2 (d, J_{CP} 10.2, *o*), 130.5 (s, *p*), and 128.2 (d, J_{CP} 10.0, *m*),[27] C_9H_7 at[24] 129.1, 127.9 (2 s, C-4,7), 126.9, 124.6 (2 s, C-5,6), 117.2, 113.7 (2 s, C-3a, 7a), 87.4 (s, C-2) and 73.4 (one s, C-1,3); $^{31}P\{^1H\}$ (ppm) 15.3 (s).

Preparation of 5 from 13. A Schlenk flask was charged with $CuBr{\cdot}S(CH_3)_2$ (0.259 g, 1.25 mmol), THF (5 mL), and a stir bar and was cooled to 0 °C. Then CH_3MgBr (0.143 mL, 2.80 M in ether, 0.400 mmol) was added with stirring to generate $CuCH_3$. After 0.5 h, a solution of **13** (0.144 g, 0.199 mmol) in THF (5 mL) was added via cannula with stirring. After 1 h, the cold bath was removed, and after an additional 2 h, the mixture was filtered through Celite. Solvent was removed from the filtrate under oil pump vacuum, and the residue was chromatographed on silica gel with CH_2Cl_2. Solvent was removed from the bright orange eluate under oil pump vacuum to give **5** as an orange solid (0.075 g, 0.123 mmol, 62%). The IR and $^1H/^{31}P$ NMR spectra were identical with those reported above.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$. A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (3.00 g, 7.08 mmol),[14] PPh_3 (5.57 g, 21.2 mmol), $ClCH_2CH_2Cl$ (80 mL), and a stir bar and was fitted with a condenser. The suspension was stirred under vacuum, saturated with N_2, refluxed in a 100 °C oil bath for 3 h, cooled to room temperature, and added to THF (300 mL). After 2 h, the resulting yellow precipitate was collected by filtration, washed with THF (3 × 3 mL), and dried under oil pump vacuum to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (3.99 g, 6.06 mmol, 86%). The IR and ^1H NMR spectra were identical with those previously reported.[14] $^{31}P\{^1H\}$ NMR (ppm, CD_3CN): 11.8 (s).

Acknowledgment. We thank the NSF for support of this research and Dr. Y. Liu for some preliminary experiments.

OM930357U