ORGANOMETALLICS

Volume 9, Number 9, September 1990

Communications

Synthesis of Cationic (π-Allyl)rhenium Complexes and Their Reactions with Carbon Nucleophiles

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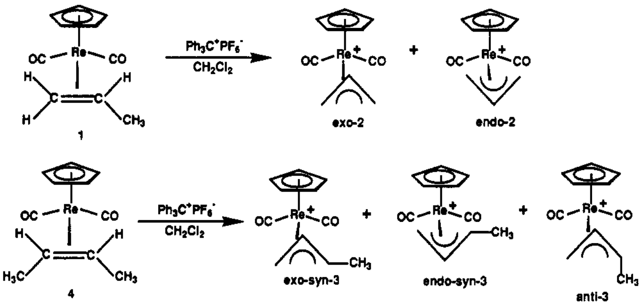
Received January 22, 1990

Summary: The cationic (π-allyl)rhenium complexes $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCH_2)^+PF_6^-$ (**2**) and $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCHCH_3)^+PF_6^-$ (**3**) were synthesized from rhenium alkene complexes $C_5H_5(CO)_2Re(\eta^2\text{-}CH_2{=}CHCH_3)$ (**1**) and $C_5H_5(CO)_2Re(\eta^2\text{-}cis\text{-}CH_3CH{=}CHCH_3)$ (**4**) by hydride abstraction with $(C_6H_5)_3C^+PF_6^-$. Allyl complexes **2** and **3** reacted with carbon nucleophiles to produce elaborated rhenium alkene complexes.

The addition of carbon nucleophiles to (η^3-allyl)metal complexes of Pd,[1] Mo,[2] and Fe[3] has been developed into an extremely useful method in organic synthesis. Here we describe the synthesis of stable (η^3-allyl)rhenium complexes from rhenium alkene complexes and their reactions with carbon nucleophiles to produce stable elaborated rhenium alkene complexes.

Hydride abstraction from rhenium alkene complexes provides a convenient, high-yield route to (η^3-allyl)rhenium complexes. Addition of $Ph_3C^+PF_6^-$ (700 mg, 2.5 mmol) to a CH_2Cl_2 solution of the rhenium complex $C_5H_5(CO)_2Re(\eta^2\text{-}CH_2{=}CHCH_3)$ (**1**;[4] 800 mg, 2.5 mmol) gave a purple solution from which a brown solid precipitated over 5 h. Solvent was evaporated, and the residue was washed several times with diethyl ether and recrystallized from acetone–diethyl ether to give the cationic (η^3-allyl)rhenium complex $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCH_2)^+PF_6^-$ (**2**; 85% yield) as a brown solid.[5] The ^{1}H NMR spectrum of **2** in DMSO-d_6 at room temperature showed the presence of a 75:25 mixture of exo and endo rotational isomers. The major isomer was tentatively assigned as the exo configuration on the basis of NMR chemical shift arguments.[6] Variable-temperature NMR spectra established that the two isomers were in rapid equilibrium. Coalescence of the syn proton signals at δ 3.90 for the major isomer and δ 3.68 for the minor isomer occurred at 70 °C, and an averaged spectrum was observed at 112 °C. Simulation of the temperature-dependent NMR spectra between 23 and 112 °C with use of DNMR5 gave rate constants for the interconversion of *exo*- and *endo*-**2**. The rotational barrier for conversion of *endo*- to *exo*-**2** was calculated to have $\Delta G^{\ddagger} = 16.5$ kcal mol^{-1} at 73 °C ($\Delta H^{\ddagger} = 13.7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -8.1$ eu).



Similarly, the (η^3-methallyl)rhenium complex $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCHCH_3)^+PF_6^-$ (**3**)[5] was obtained in

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[1] (a) Trost, B. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 57. (b) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (c) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

[2] (a) Van Arsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645. (b) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570. (c) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937.

[3] (a) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63. (b) Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5792. (c) Roustan, J. L.; Merour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721. (d) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. (e) Eberhardt, U.; Mattern, G. *Chem. Ber.* **1988**, *121*, 1531.

[4] Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917.

[5] See the supplementary material for complete characterization of compounds.

[6] Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

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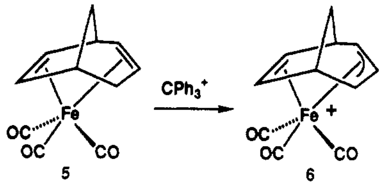
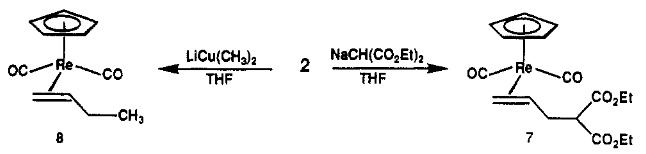
62% yield from the reaction of $C_5H_5(CO)_2Re(\eta^2$-*cis*-$CH_3CH{=}CHCH_3)$ (4)[4] with $Ph_3C^+PF_6^-$. The ^1H NMR spectrum of **3** in acetone-d_6 showed the presence of three isomers, *exo-syn*-**3**, *endo-syn*-**3**, and *anti*-**3** in a 62:29:9 ratio. Direct hydride abstraction from the *cis*-2-butene complex should have produced only *anti*-methallyl complexes. The predominant formation of *syn*-methallyl complexes requires an isomerization, possibly via a σ-allyl intermediate or alternatively by reversible addition of a weak nucleophile to the more substituted allyl carbon.

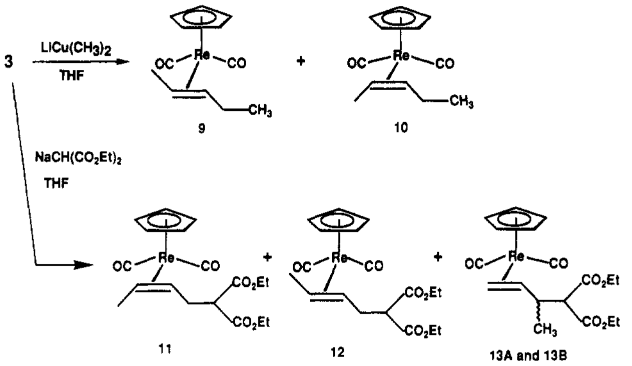
The only previous report of the generation of a (π-allyl)metal complex by hydride abstraction from an alkene complex is the conversion of iron diene complex **5** to the iron alkene-π-allyl complex **6** reported by Rosenblum.[7] In other related chemistry, Fischer reported the synthesis of (η^5-cyclohexadienyl)$Fe(CO)_3^+$ by hydride abstraction from (η^4-cyclohexadiene)$Fe(CO)_3$.[8]



The cationic (π-allyl)rhenium complexes **2** and **3** readily reacted with organic nucleophiles to produce neutral elaborated rhenium alkene complexes. A slurry of the rhenium allyl complex **2** (100 mg, 0.20 mmol) and sodium diethyl malonate (37 mg, 0.20 mmol) in THF was stirred for 5 h. After evaporation of solvent, the residue was chromatographed (silica gel, hexane–ether) to give $C_5H_5(CO)_2Re[\eta^2\text{-}CH_2{=}CHCH_2CH(CO_2Et)_2]$ (**7**; 89 mg, 90%) as a colorless liquid.[5] Similarly, addition of $LiCu(CH_3)_2$ (0.20 mmol) to a THF solution of **2** (100 mg, 0.20 mmol) led to the isolation of $C_5H_5(CO)_2Re(\eta^2\text{-}CH_2{=}CHCH_2CH_3)$ (**8**;[5] 56 mg, 76%).



Predominant addition to the less substituted allyl carbon was observed in the addition of $LiCu(CH_3)_2$ (0.20 mmol) (53 mM, 1.87 mL) to **3** (100 mg, 0.20 mmol), which produced a 65:35 mixture of $C_5H_5(CO)_2Re[\eta^2$-*trans*-$CH_3CH{=}CHCH_2CH_3]$ (**9**)[5] and $C_5H_5(CO)_2Re[\eta^2$-*cis*-$CH_3CH{=}CHCH_2CH_3]$ (**10**)[5] in 50% combined yield. The coupling constant between the vinylic hydrogens of **9** (J = 10.2 Hz) was slightly larger than in the case of **10** (J = 9.0 Hz); therefore, **9** was tentatively assigned as the trans isomer and **10** was assigned as the cis isomer. Stereospecific addition of $LiCu(CH_3)_2$ to **3** (91:9 syn:anti) should have produced a similar ratio of trans isomer **9** to cis isomer **10**, but only a 65:35 ratio of **9** to **10** was observed. This suggests that some syn to anti isomerization is occurring prior to or during nucleophilic addition to **3**. We are confident that the alkene isomers **9** and **10** do not isomerize after formation, since we have shown that the *cis*-2-butene complex **4** was not isomerized by $LiCuMe_2$.



Some regioselectivity for addition of malonate to the less substituted allyl carbon of the (methallyl)rhenium complex **3** was also observed. Reaction of **3** (200 mg, 0.39 mmol) with sodium diethyl malonate (70 mg, 0.39 mmol) in THF gave a 92% yield of a mixture of $C_5H_5(CO)_2Re[\eta^2$-*cis*-$CH_3CH{=}CHCH_2CH(CO_2Et)_2]$ (**11**), $C_5H_5(CO)_2Re[\eta^2$-*trans*-$CH_3CH{=}CHCH_2CH(CO_2Et)_2]$ (**12**), and two diastereomers of $C_5H_5(CO)_2Re[\eta^2\text{-}CH_2{=}CHCH(CH_3)CH(CO_2Et)_2]$ (**13A** and **13B**) in a ratio of 54:6:25:15.[5] The stereochemistries of cis isomer **11** (J = 9.3 Hz) and of trans isomer **12** (J = 10.2 Hz) were tentatively assigned on the basis of the vinylic coupling constants in the ^1H NMR spectra. If this assignment is correct, then the formation of a 54:6 ratio of cis isomer **11** to trans isomer **12** from a 91:9 ratio of *syn*-**3** to *anti*-**3** requires substantial syn/anti isomerization of **3** during the course of nucleophilic addition.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Spectral and characterization data for compounds **2**, **3**, and **7–13** (4 pages). Ordering information is given on any current masthead page.

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(8) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919.