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Hydroxycarbenoid Complexes Derived from a Catalytic Olefin Metathesis System

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Catalytic olefin metathesis has been widely studied in recent years [1]. It is now generally accepted that carbenoid metal complexes are actively involved in many, if not all, such systems. However, it often remains unclear how the carbenoid complexes are generated from the precursor alkyl- and/or halometal complexes. We have explored the initial interaction of $ReCl(CO)_5$ with $AlCl_2(C_2H_5)$, the combination of which is catalytically active for olefin metathesis [2]. The recent report [3] of the synthesis of the hydroxycarbenoid complex *cis*-$ReCl[C(CH_3)(OH)](CO)_4$, *1*, prompts us to communicate that similar complexes may be prepared by hydrolysis (or methanolysis) of the catalytic system described above or related systems.

Results and Discussion

The treatment of $Re(CH_3)(CO)_5$ with two equivalents of $AlCl_2(C_2H_5)$ in chlorobenzene at room temperature results in the replacement of the singlet in the ^1H nmr spectrum due to $Re(CH_3)(CO)_5$ (δ 0.1) with a new singlet at δ 2.9. In addition, multiplets are present at δ 1.4(t) and δ 0.6(q) arising from the methyl and methylene hydrogen atoms, respectively, derived from $AlCl_2(C_2H_5)$. The use of only one equivalent of $AlCl_2(C_2H_5)$ results in conversion of *one-half* of the $Re(CH_3)(CO)_5$ to the new species. The 1:2 mixture is catalytically active for metathesis of primary olefins and resembles the system derived from $ReCl(CO)_5$ and *three* equivalents of $AlCl(C_2H_5)$ [2].

Exposure of the 1:2 mixture to moist air or dropwise treatment with methanol results in the separation of a white solid. Removal of solvent from the yellow filtrate leads to the isolation of white crystals of *1* in moderate yield. Similarly, $Re(C_6H_5)(CO)_5$ may be treated with two equivalents of $AlCl_2(C_2H_5)$ (also giving an active catalyst) which upon hydrolysis leads to the isolation of the more thermally stable yellow complex *cis*-$ReCl[C(C_6H_5)(OH)](CO)_4$, *2*. Both *1* and *2* exhibit low field ^1H nmr resonances assignable to the hydroxy-proton. A very broad, temperature dependent resonance at δ 16.1 is found for *1* while a much sharper peak at δ 16.2 is observed for *2*. The dramatic shift to low field supports the proposal of intramolecular hydrogen bonding in such systems [4].

The treatment of $ReCl(CO)_5$ with three equivalents of $AlCl_2(C_2H_5)$ followed by methanolysis yields a yellow oil which is less thermally stable than *1* or *2*. Spectroscopic data suggest that it is *cis*-$ReCl[C(C_2H_5)(OH)](CO)_4$, *3*.

The complexes *1–3* themselves are not active as olefin metathesis catalysts. Furthermore, treatment with $AlCl_2(C_2H_5)$ does not regenerate an active catalyst.

Experimental

All reactions were carried out under dinitrogen. Nmr and catalytic studies as well as the initial isolation of products were accomplished using chlorobenzene as solvent. Better yields of products were obtained by carrying out reactions in and isolating products from lower boiling hydrocarbon solvents.

cis-*ReCl[C(CH*$_3$*)(OH)](CO)*$_4$, 1

A solution of $Re(CH_3)(CO)_5$ (0.63 g, 1.85 mmol) in cyclohexane (40 cm^3) was treated with $AlCl_2(C_2H_5)$ (0.50 g, 3.9 mmol) at 50 °C for one-half hour. The mixture was cooled to room temperature and moist air bubbled through it for one-half hour. Filtration, concentration and cooling to –20 °C resulted in the formation of white crystals of *1* (0.23 g, 35% yield), m.p. 78 °C d. Calculated for $[C_6H_4ClO_5Re]$: C, 19.07; H, 1.06; Cl, 9.39. Found: C, 19.54; H, 1.07; Cl, 9.32%. ^1H nmr (C_6D_6) δ 2.1(s), 16.1 (very broad); ir ν_{CO} (hexane) 2110w, 2029m, 2016s, 1947s cm^{-1}. Mass spectroscopy revealed an isotopic pattern centered at m/e 377, typical for the presence of one rhenium atom and one chlorine atom. This peak corresponds to the parent ion less one hydrogen atom.

cis-*ReCl[C(C*$_6$*H*$_5$*)(OH)](CO)*$_4$, 2

$Re(C_6H_5)(CO)_5$ (0.95 g, 2.3 mmol) in chlorobenzene (10 cm^3) was treated with $AlCl_2(C_2H_5)$ (0.60 g, 4.7 mmol) at room temperature. The temperature was raised to 90 °C, causing a color change from yellow to brown. After 15 minutes, 1,7-octadiene (1 cm^3) was added and metathesis began, as evidenced by the evolution of ethylene (nmr) and the formation of cyclohexene (glc). After 5 minutes

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of reaction, the mixture was cooled and all volatile material removed under high vacuum. Light petroleum b.p. 40–60 °C (50 cm^3) was re-added to the residue and the yellow solution treated with methanol (1 cm^3), causing a white solid to precipitate. Filtration and concentration led to the isolation of yellow crystals of *2* (0.50 g, 49%), m.p. 94 °C. Calculated for $[C_{11}H_6ClO_5Re]$: C, 30.04; H, 1.37; Cl, 8.07. Found: C, 30.14; H, 1.41; Cl, 7.90%. ^1H nmr (C_6D_6) δ 6.9 (m, 3), 7.6 (m, 2), 16.2 (broad); ir ν_{CO} (hexane) 2109w, 2026m, 2015s, 1945ms cm^{-1}. The mass spectrum again revealed a parent ion less one hydrogen atom.

Reaction of $ReCl(CO)_5$ with $AlCl_2(C_2H_5)$

$ReCl(CO)_5$ (0.65 g, 1.8 mmol) was suspended in cyclohexane (80 cm^3) and treated with $AlCl(C_2H_5)$ (1.0 g 7.9 mmol) and heated at reflux for one hour. The mixture was cooled to room temperature and treated with methanol. The resulting white solid was separated by filtration and the yellow filtrate was concentrated to yield a pale yellow oil (*3*) which is thermally and hydrolytically unstable. ^1H nmr (C_6D_6) δ 0.6 (t, 3, J = 7 Hz), 2.6 (q, 2); ir ν_{CO} (hexane) 2109w, 2028m, 2015s, 1946s cm^{-1}.

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