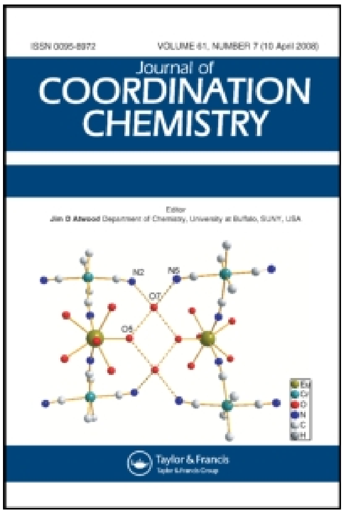

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SYNTHESIS AND CHARACTERIZATION OF RHENIUM ISOCYANATE COMPLEXES (η-C_5Me_5)Re(CO)$_2$(NCO)X, X = Cl, Br and I

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Reactions of the tricarbonylrhenium halide cations $[Cp^*Re(CO)_3X]^+$ ($Cp^* = \eta^5$-C_5Me_5, X = Cl, Br and I) with azide ion are described, leading to dicarbonylisocyanate complexes *trans*-$Cp^*Re(CO)_2(NCO)X$. The *trans* orientation of the carbonyl groups in these complexes was assigned by IR spectroscopy and by comparison with the known complexes $Cp^*Re(CO)_2X_2$ and $Cp^*Re(CO)_2(COOR)(X)$. Some details concerning the mechanism of the formation of only one isomer is also included.

Keywords: Isocyanate, rhenium, complexes, synthesis

INTRODUCTION

In previous papers, we reported synthetic[1] and spectroscopic[2] studies of a series of (pentamethylcyclopentadienyl)dicarbonylrhenium halide cations $[Cp^*Re(CO)_3X]^+$ ($Cp^* = \eta^5$-C_5Me_5; X = Cl, Br and I). We have also described the reactions of these cations with alkoxide ions leading to the alkoxycarbonyl complexes *trans*-Cp* Re(CO)$_2$(COOR)X (X = Cl and Br, R = Me and X = I, R = Me, Et and Pr).[3]

As part of our continuing studies of transformations of coordinated CO ligands of rhenium fragments, we now wish to report the results of nucleophilic attack of N_3^- on a carbonyl group of the cationic $[Cp^*Re(CO)_3X]^+$ complexes. At the same time, we hoped to obtain some insight into isocyanate complexes, since relatively few examples have been isolated and characterized despite their proposed intermediacy in catalytic reactions such as that of nitrogen oxides with carbon monoxide over heterogeneous catalysts,[4] and olefin hydrogenation.[5] Some examples of isocyanate complexes are CpFe(CO)$_2$(NCO), ($Cp = \eta^5$-C_5H_5),[6] CpFe-(CO)(C_2H_4)(NCO),[7] (arene)Mn(CO)$_2$ (NCO) (arene = C_6Me_6 and mesitylene),[8] Cp or Cp*Re(CO)(N_2Ar)(NCO)[9] and $[LRe(NO)(CO)(NCO)]^+$ (L = 1,4,7-triazacyclononane).[10] Very recently, Beck published a review related to reactions of metal-carbonyl complexes with azide.[11]

EXPERIMENTAL

All manipulations were carried out under nitrogen using Schlenk techniques. IR spectra were measured in solution (KBr cells) on Perkin-Elmer 599 or 983 instru-

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ments. ^1H and ^{13}C NMR spectra (Brucker WM 400), mass spectra (Hewlett-Packard 5985) and elemental analysis were obtained using the facilities of Chemistry Department, Simon Fraser University, Canada.

Solvents were distilled under nitrogen prior to use, and NaN_3 (Aldrich) was used as received. The cationic complexes $[Cp^*Re(CO)_3X]^+$ were prepared according to literature procedures.[1]

Preparation of trans-*$Cp^*Re(CO)_2(I)(NCO)$* (1)

The cationic complex $[Cp^*Re(CO)_3I]I_3$ (100 mg) was dissolved in 10 cm^3 of CH_3CN at room temperature. To this red solution an excess of solid NaN_3 (15 mg) was added with stirring. After about 1 hr the IR spectrum showed the disappearance of the cationic complex and the presence of the isocyanate complex. The solvent was pumped off and the red-brown residue extracted with diethyl ether and filtered through Celite. The red solid obtained after ether evaporation was chromatographed on a neutral alumina column. The column was washed with hexane and the product then eluted with ether. Removal of the ether under vacuum resulted in a red solid. Recrystallization from CH_2Cl_2/hexane (1:5) at −15°C gave (1) (40 mg) as dark red microcrystals in 70% yield. The compound decomposed above 80°C. Elemental analysis ($C_{13}H_{15}NO_3IRe$); calculated: C, 28.57; H, 2.74; N, 2.56%. Found: C, 28.55, H, 2.80; N, 2.53%. MS (electron impact, based on ^{187}Re) *m/z* 547 (M^+), 519 (M^+-CO), 505 (M^+-NCO), 491 (M^+-2CO). IR (CH_2Cl_2, cm^{-1}): 2254 (vs) (ν NCO), 2052 (s) and 1987 (vs) (ν CO). ^1H NMR ($CDCl_3$) δ 2.099 (s, C_5Me_5); $^{13}C\{H\}$ NMR ($CDCl_3$): δ 11.05 (s, $C_5\mathit{Me}_5$), 105.18 (s, C_5Me_5), 185.84 (s, CO).

Preparation of trans-*$Cp^*Re(CO)_2(Br)(NCO)$* (2)

A procedure similar to that described for the above compound, except that the chromatographic elution was carried out using a mixture of CH_2Cl_2/hexane (1:1), gave the bromoisocyanate complex (2) as a red microcrystalline solid in 52% yield. This compound starts to decompose above 75°C. Elemental analysis ($C_{13}H_{15}NO_3BrRe$); calculated: C, 31.30; H, 3.05; N, 2.80%. Found: C, 31.60; H, 3.20; N, 2.70%. IR (CH_2Cl_2, cm^{-1}): 2245 (vs) (ν NCO), 2060 (s) and 1992 (vs) (ν CO). ^1H NMR ($CDCl_3$); δ 1.987 (s, C_5Me_5); $^{13}C\{H\}$ NMR ($CDCl_3$): δ 10.03 (s, $C_5\mathit{Me}_5$), 106.08 (s, C_5Me_5), 187.84 (s, CO).

Preparation of trans-*$Cp^*Re(CO)_2(Cl)(NCO)$* (3)

This complex was synthesized similarly to those previously described, but a mixture of CH_2Cl_2/THF (3:1) was used as reaction solvent. The chromatographic purification was carried out on silica gel 60 (Merck) and the compound eluted with ether. After crystallization from CH_2Cl_2/hexane, the chloroisocyanate derivative (3) was obtained as a dark red solid in 38% yield. The complex decomposed above 68°C. Elemental analysis ($C_{13}H_{15}NO_3ClRe$): calculated: C, 34.30; H, 3.30; N, 3.10%. Found: C, 33.01; H, 3.39; N, 2.95%. IR (CH_2Cl_2, cm^{-1}): 2247 (vs) (ν NCO), 2066 (s) and 1994 (vs) (ν CO). ^1H NMR ($CDCl_3$, 60 MHz Varian EM-306A): δ 1.93 (s, C_5Me_5).

RESULTS

The *trans*-isocyanate complexes $Cp^*Re(CO)_2(NCO)X$, X = I (**1**), Br (**2**) and Cl (**3**), were prepared by the reaction of the cationic tricarbonyl complexes $[Cp^*Re(CO)_3X]^+$ in CH_3CN or CH_2Cl_2/THF with azide ion (N_3^-), (*1*).

$$[Cp^*Re(CO)_3X]^+ + N_3^- \longrightarrow trans\text{-}Cp^*Re(CO)_2(NCO)X \qquad (1)$$

These red or red-brown microcrystalline solids are indefinitely stable under N_2 at −10°C and appear not to deteriorate when exposed to air over a period of hours. The complexes are thermally stable as solids up to about 70°C whereupon they decompose without melting. They are very soluble in polar organic solvents such as acetone, $CHCl_3$, CH_2Cl_2 or THF. In these solvents they appear not to undergo isomerization at room temperature, though they do not survive under these conditions for more than 5 hours, the most stable being the iodo derivative. The observed decomposition products (by IR) are the corresponding $Cp^*Re(CO)_2X_2$ species, among other unidentified carbonyl-containing complexes. $Cp^*Re(CO)_2Cl_2$ was the only product identified by ^1H and ^{13}C NMR during an overnight run in $CDCl_3$ solution of complex (**3**).

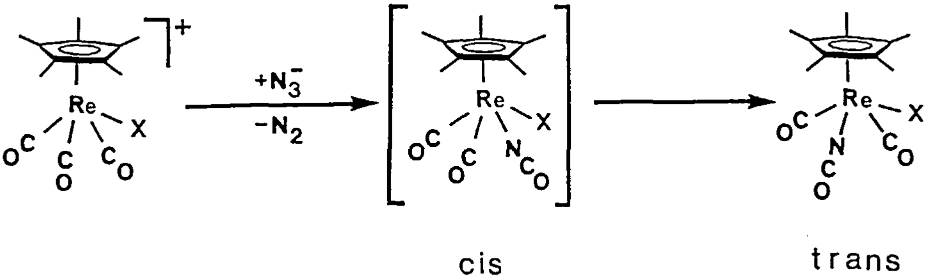
Attempts to isomerize these isocyanate complexes, thermally (boiling toluene) or photochemically (THF solution, UV light), were unsuccessful since the complexes decomposed very readily under these conditions.

Spectroscopic measurements of the complexes clearly indicate the presence of a single isomer. Thus, there is a single set of ν(NCO) and ν(CO) absorptions near 2245, and 2060 and 1980 cm^{-1} respectively, in the IR spectra, and a single resonance at about 2.0 ppm for the Cp* ligand in the ^1H NMR spectra. The two complexes studied by ^{13}C NMR show the expected resonances for Cp* (at about 10.0 and 105.0 ppm) and a low field singlet (~186.0 ppm) for the two equivalent CO groups. However, they do not show the resonance for the –NCO carbon expected at about 130 ppm.[10,12] The mass spectra show the molecular ion only for the more stable iodo derivative (**1**); in addition, it shows fragments due to the $Cp^*Re(CO)_2I_2$ complex. The chloro (**3**) and bromo (**2**) compounds do not show any parent peak even at 14 eV. Instead, the spectra show the presence of the dihalide complexes $Cp^*Re(CO)_2X_2$, X = Cl and Br, respectively.

DISCUSSION

The formation of the dicarbonylisocyanate complexes *trans*-Cp^* $Re(CO)_2$ (X) (NCO) from the tricarbonyl cations $[Cp^*Re(CO)_3X]^+$ (*1*), is expected considering Angelici's prediction, that is, carbonyl-containing compounds with ν(CO)- > 2000 cm^{-1} should yield the transformation of a coordinated CO ligand, when they react with nucleophiles.[13] We presume that the mechanism of these reactions is analogous to those proposed for the very similar reaction of $[CpFe(CO)_3]^+$ with N_3^-, leading to $CpFe(CO)_2(NCO)$.[6] It probably involves initial attack of the nucleophile at a coordinated carbonyl carbon atom. However, in our cationic precursors possessing a four-legged piano stool type of structure, there are two types of CO ligand susceptible to nucleophillic attack, thus leading to two distinct isomers. The exclusive appearance of the *trans* isomer in these complexes (*vide infra*) as well as in the alkoxycarbonyl derivatives *trans*-$Cp^*Re(CO)_2$

(COOR)(X),[3] encouraged us to undertake a complete vibrational analysis of $[Cp^*Re(CO)_3X]^+$.[2] Based on this study, we found that the force constant of the CO group *trans* to the halide ligand has the lowest value when compared with the force constant of the two equivalent CO groups *cis* to the halide ($f_{CO}(trans) \cong 15.2$, $f_{CO}(cis) \cong 16.0$ mdy/Å). According to Angelici,[13] the latter should be the more reactive toward nucleophiles, leading in this case to *cis*-$Cp^*Re(CO)_2(X)(NCO)$. However, the isolation of only the *trans* isomer indicates that the *cis* attack can be viewed as a kinetic product which in turn isomerizes, thermally or photochemically, to the more stable *trans* isomer (see Scheme I).



Evidence for the stereochemistry of the isocyanate complexes could be readily inferred from the relative intensities of the ν(CO) absorptions. In all cases, the intensity of the symmetric CO stretching vibration ν_s(CO) (at higher frequency) is about half that of the antisymmetric vibration ν_{as}(CO) (at lower frequency). This could be an indication that these compounds, possessing a four-legged piano stool structure, are the *trans* or diagonal isomers. A similar intensity ratio (ν_s:ν_{as}) has been observed in *trans*-$Cp^*Re(CO)_2(X)(COOR)$ (1:1.7)[3] and *trans*-$Cp^*Re(CO)_2Br_2$ (1:1.8).[14] For the latter compound, the stereochemistry was established by X-ray crystallography.

The presence of the coordinated isocyanate ligand in these complexes could be easily observed *via* a strong absorption at about 2245 cm^{-1} in the IR spectra. This value is in good agreement with the frequencies for this group observed in other related complexes.[6-10] The absence of the ^{13}C resonance for the NCO carbon in the ^{13}C NMR spectra of these complexes, expected to occur at about 130 ppm, can be attributed to a combination of factors including quadrupolar broadening, large T_1 values and the absence of an Overhauser effect.[15]

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