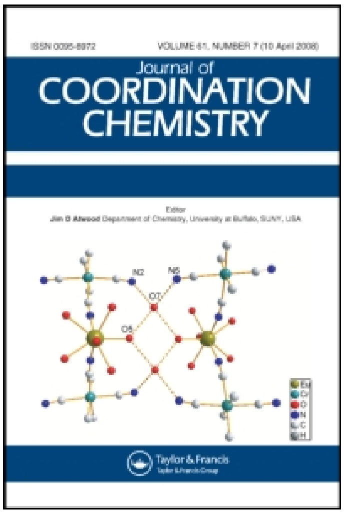

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SHORT COMMUNICATION

Preparation of [Monohydrogen Mesoporphyrin IX Dimethyl Esterato]tricarbonyltechnetium(I) and its Novel Thermal Disproportionation[1]

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A novel thermal disproportionation (unusual coordination phenomenon) of monotechnetium mesoporphyrin IX dimethyl ester, $HMPTc(CO)_3$, a new metalloporphyrin, to ditechnetium mesoporphyrin, $MP[Tc(CO)_3]_2$, and free mesoporphyrin IX dimethyl ester is reported.

Recent progress in the chemistry of synthetic metalloporphyrins has shown that the porphyrin moiety can act as a bi-, tri-, or hexadentate ligand[1–6] as well as the usual tetradentate ligand.[7–8] The first example of a tridentate porphyrin ligand is [monohydrogen mesoporphyrin IX dimethyl esterato] tricarbonylrhenium(I), $HMPRe(CO)_3$. This compound can further react with dirhenium decacarbonyl, $Re_2(CO)_{10}$, to form μ-[mesoporphyrin IX dimethyl esterato] bis [tricarbonylrhenium(I)], $MP[Re(CO)_3]_2$, the first example of a hexadentate porphyrin ligand.[3–5] We wish to report the preparation of the first example of a monotechnetium porphyrin, [monohydrogen mesoporphyrin IX dimethyl esterato] tricarbonyltechnetium(I), $HMPTc(CO)_3$, and its novel thermal disporportionation.

Mesoporphyrin IX dimethyl ester,[9] $H_2MPIXDME$, and ditechnetium decacarbonyl,[10] $Tc_2(CO)_{10}$, in 1 to 0.6 mole ratio were mixed in decalin[11] and heated under argon in a 150° oil-bath for two hours. Completion of the reaction was determined by visible spectroscopy. When absorptions at 387 (soret) and 470 nm reached maxima, the reaction was stopped. The decalin solution was cooled, centrifuged, and decanted, and the supernatant evaporated to dryness under vacuum. The resulting solid was then dissolved in benzene and chromatographed on a talc column. Three bands were eluted from the column by benzene/cyclohexane (50/50), dichloromethane, and acetone respectively. A small amount of chocolate colored material was followed by a large pale green band; and finally by a small amount of red compound. Visible spectroscopy showed the first and the third bands to be μ-[mesoporphyrin IX dimethyl esterato] bis [tricarbonyltechnetium(I)],[6] $MP[Tc(CO)_3]_2$, and mesoporphyrin IX dimethyl ester, $H_2MPIXDME$. Dichloromethane solution of the second band was evaporated to small volume under a stream of nitrogen, centrifuged, and decanted. The supernatant was evaporated to dryness and washed with n-pentane to give an air stable, dark brown solid, **I**, mp 181–182°. Anal.[12] Calcd. for $TcC_{39}H_{41}N_4O_7$: N, 7.22; Tc, 12.75; Mol. Wt., 776.8. Found: N, 7.34; Tc, 13.98; Mol. Wt., 767 (measured by vapor pressure osmometry in chloroform). The solid **I** in dichloromethane gave a light green solution with visible absorptions at 580 nm (log ϵ, 3.174), 470 (3.699), and 387 (4.126). The infrared spectrum of **I** in the solid phase (KBr) showed an absorption at 3380 cm^{-1} (N–H stretch); three strong metal-carbonyl stretching bands at 2025, 1920 and 1900 cm^{-1}; and a sharp ester carbonyl peak at 1735 cm^{-1}. The proton magnetic resonance (pmr) spectrum of **I** in deuteriochloroform was that of a complexed porphyrin with the addition of a broad ($W_{1/2}$ = 6 cps) peak at τ 14.9, corresponding to a single proton; addition to the $CDCl_3$ solution of a small amount of DCl in D_2O caused the immediate disappearance of this peak. This phenomenon is same as that observed for $HMPRe(CO)_3$ in a previous report. This indicates that the proton observed is bonded to the porphyrin nitrogen instead of the metal atom.[3] Structure **I**, shown in Figure 1, is proposed for $HMPTc(CO)_3$ in analogy to $HMPRe(CO)_3$[3–5] and [monohydrogen meso-tetrapheylporphinato] tricarbonylrhenium(I),[13] $HTPPRe(CO)_3$. Unexpectedly, when this

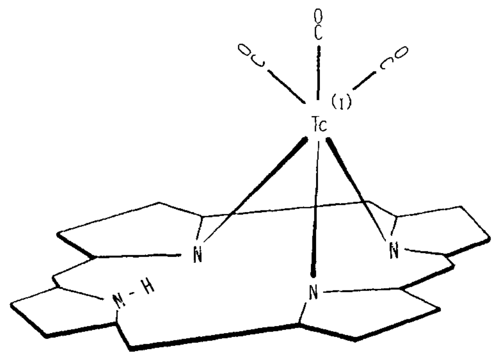

FIGURE 1 Schematic picture of HMPTc(CO)$_3$, I; the alkyl substituents on the porphine ring are omitted for clarity.

same reaction between Tc$_2$(CO)$_{10}$ and H$_2$MPIXDME was run at reflux, 193.3°, in decalin for four hours, the reaction products were MP[Tc(CO)$_3$]$_2$, **II**, and H$_2$MPIXDME, but not HMPTc(CO)$_3$, **I**. The results of these two reactions suggest that Tc$_2$(CO)$_{10}$ and HP$_2$MPIXDME react initially to form HMPTc(CO)$_3$, **I** which then disproportionates into MP[Tc(CO)$_3$]$_2$, **II**, and H$_2$MPIXDME.

The formation of HMPTc(C)$_3$, **I**, as an initial reaction product between Tc$_2$(CO)$_{10}$ and H$_2$MPIXDME was also observed[6] even though metal carbonyl was used in a ratio of 1.2 to 1, Tc$_2$(CO)$_{10}$ to H$_2$MPIXDME. This behavior was confirmed by heating a benzene/dichloromethane (50/50) solution of **I** to dryness in a hot-water bath at 50–60°; trace amount of both MP[Tc(CO)$_3$]$_2$ and H$_2$MPIXDME were separated by talcum column again. This clearly demonstrates that upon heating HMPTc(CO)$_3$, **I**, disproportionates to give MP[Tc(CO)$_3$]$_2$, **II**, and H$_2$MPIXDME (Figure 2).

Such a reaction was not observed on heating HMPRe(CO)$_3$ in decalin.[3,5] However, it seems that MP[*M*(CO)$_3$]$_2$ is thermodynamically more stable than HMP*M*(CO)$_3$, (*M* = Re or Tc), because a reverse reaction of MP[*M*(CO)$_3$]$_2$ to HMP*M*(CO)$_3$[3,5] could not be detected between MP[*M*(CO)$_3$]$_2$ and H$_2$MPIXDME in refluxing decalin for either the rhenium or technetium dimetalloporphyrins.

MP[Tc(CO)$_3$]$_2$, **II**, was stable at room temperature but it was thermally unstable[6] in refluxing decalin in a different manner than HMPTc(CO)$_3$, **I**. When a decalin solution of **II** was refluxed under argon for more than four hours, a large amount of solid material precipitated from the decalin. The unknown solid compound, **III**, was insoluble in most organic solvents but was slightly soluble in dichloromethane, revealing a sharp visible absorption peak at 358 nm with three broad weak peaks at 397 (soret), 500 and 540 nm. The unknown **III** turned black above 260° without melting. The infrared spectrum of the unknown **III** in the solid phase (KBr) showed two strong metal-carbonyl stretches at 2044 and 1925 cm^{-1} and a split sharp ester carbonyl peak centered at 1725 cm^{-1}. A similar splitting of an ester carbonyl peak has been observed in solid MPRuCO[14] and tentatively assigned to coordination between the ester carbonyl and the metal. The unknown solid, **III**, may be a coordination polymer involving similar coordination between a metal and an ester carbonyl.

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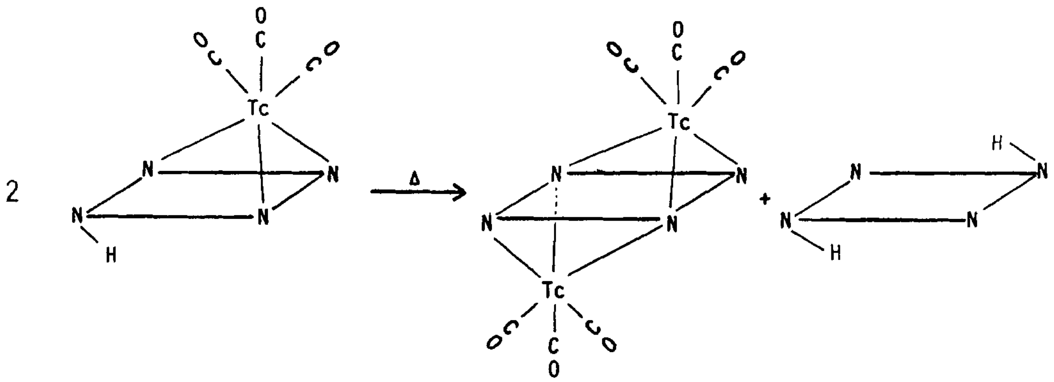

I

II

FIGURE 2 Disproportionation of HMPTc(CO)$_3$,I.

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