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PHOTOCHEMICAL REACTIONS OF TRANSITION-METAL DINITROGEN COMPOUNDS IN THE PRESENCE OF CARBON MONOXIDE

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It is well known that transition-metal carbonyl compounds readily undergo photolysis resulting in loss of the carbon monoxide ligand. However, no analogous photochemical studies on transition-metal compounds containing the isoelectronic dinitrogen ligand have thus far been reported.

We have been studying the photochemistry of the dinitrogen complexes of Re(I), Fe(II), Os(II) and Mo(O) in the presence of excess carbon monoxide and our results are the following:

(1) $\mathrm{ReCl(N_2)(PMe_2Ph)_4} + \mathrm{CO} \xrightarrow{h\nu} \underline{\mathrm{cis}}\ \mathrm{ReCl(CO)_2(PMe_2Ph)_3}$

(2) $\mathrm{FeH_2(N_2)(PEtPh_2)_3} + \mathrm{CO} \xrightarrow{h\nu} \mathrm{Fe(CO)_4(PEtPh_2)}$

$+ \underline{\mathrm{trans}}\ \mathrm{Fe(CO)_3(PEtPh_2)_2}$

(3) $\mathrm{OsCl_2(N_2)(PEt_2Ph)_3} + \mathrm{CO} \xrightarrow{h\nu} \mathrm{OsCl_2(CO)(PEt_2Ph)_3}$

$+ \underline{\mathrm{cis}}\text{ and }\underline{\mathrm{trans}}\ \mathrm{OsCl_2(CO)_2(PEt_2Ph)_2}$

(4) $\underline{\mathrm{trans}}\ \mathrm{Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2} + \mathrm{CO} \xrightarrow{h\nu}$

$+ \underline{\mathrm{cis}}\ \mathrm{Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2}$

The starting materials were prepared according to published procedures.[1] Reactions were carried out in tetrahydrofuran in a pyrex vessel maintained below 20° by means of a water condenser. Carbon monoxide was slowly bubbled through the solution during the irradiation process. The light source was a Hanovia 550 watt mercury lamp and was externally placed about 25 cm from the reaction vessel.

For $ReCl(N_2)(PMe_2Ph)_4$ 100% conversion to the cis $ReCl(CO)_2(Me_2PhP)_3$ complex was achieved after 1 hour of irradiation. Samples taken at several time intervals during an irradiation period of 2.5 hours showed only the production of the cis-$ReCl(CO)_2(PMe_2Ph)_3$ product. This product has physical and spectral properties (m.p. 153-155°, ν_{CO} at 1933 and 1836 cm^{-1}, $\tau(CH_3)$, 8.18 (t), 8.25(t) and 8.79(d)) identical with those reported by Shaw[2] for cis $ReCl(CO)_2(PMe_2Ph)_3$ obtained by treatment of mer-$ReCl_3(PMe_2Ph)_3$ with sodium amalgam and carbon monoxide. The experiment was repeated in the presence of N_2 instead of carbon monoxide resulting in only a slight decomposition of starting material with no production of the analogous bis-dinitrogen rhenium complex.

Irradiation of $FeH_2(N_2)(PEtPh_2)_3$ for 0.5 hours led to the formation of the yellow complexes $Fe(CO)_4(PEtPh_2)$ and trans $Fe(CO)_3(PEtPh_2)_2$ in about a 1:1 ratio. These complexes were identified by their infrared spectra in hexane solution in the carbonyl stretching region; $Fe(CO)_4(PEtPh_2)$ (ν_{CO} at 2051(A_1), 1977(A_1), and 1943, 1936cm^{-1}(E mode split)), trans $Fe(CO)_3$-$(PEtPh_2)_2$ (ν_{CO} at 1887 and 1879cm^{-1}(E mode split)).
$FeH_2(N_2)(PEtPh_2)_3$ has been shown to react with carbon monoxide thermally to produce $FeH_2(CO)(PEtPh_2)_3$[1b]. $RuH_2(N_2)(PEtPh_2)_3$ similarly reacts thermally with carbon monoxide to produce $RuH_2(CO)(PEtPh_2)_3$[3]. Presumably, $FeH_2(CO)(PEtPh_2)_3$ is an inter-

mediate in the photochemical reaction described in eq. 2 since it was independently found to undergo photolysis in the presence of carbon monoxide leading to products identical to those obtained from the dinitrogen species. In a related process Chatt and co-workers[4] have observed that $OsH_2Cl_2(PEt_2Ph)_3$ reacts thermally with carbon monoxide quantitatively displacing dihydrogen to produce $OsCl_2(CO)(PEt_2Ph)_3$ and $OsCl_2(CO)_2(PEt_2Ph)_2$.

mer $OsCl_2(CO)(PEt_2Ph)_3$ (isomer II)[5] and cis and trans $OsCl_2(CO)_2(PEtPh)_2$ were produced by irradiation of $OsCl_2(N_2)(PEt_2Ph)_3$ for 0.7 hours in the presence of excess carbon monoxide.

The photochemical reaction of the trans $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ complex with carbon monoxide gave the known pale yellow dicarbonyl complex cis $Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2$[6] ($\nu_{CO}$ in $CHCl_3$ at 1850 and 1782cm^{-1}) in approximately 50% conversion after 15 min. with no trace of starting material remaining. Recently, this same reaction has been found to proceed thermally at ambiet temperatures over a 4 day period.[7] It is interesting to note that in both the photochemical and thermal reactions the dicarbonyl complex obtained has the cis configuration, while the corresponding bis-dinitrogen complex is isolated as the trans form. An additional orange-red product (ν_{CO} at 1869cm^{-1}) was obtained from the photolysis. Further irradiation of this complex in solution for an additional 0.5 hours caused a shift in ν_{CO} in the complex to 1812cm^{-1}. This product is proposed to be similar to the reddish-orange complex empirically formulated as

$Mo(CO)(PPh_3)_2$(ν_{CO} at 1820 or 1800 cm^{-1}) obtained from $Mo(N_2)(PPh_3)_2$ and carbon monoxide thermally.[7]

The above complexes have been characterized by elemental analysis, i.r., and ^1H n.m.r. spectra.

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