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The Nature of Binuclear Dinitrogen Complexes of Rhenium(I) and Rhenium(V) in Solution

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$Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ has been found to interact with $Re(O)[P(C_6H_5)_3]_2Cl_3$ and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ in chloroform solution to yield equilibrium mixtures containing bridging dinuclear Re^I-N_2-Re^V species. The equilibrium constant for this process was observed to be extremely dependent on the nature of the Re^V complex. Infrared intensity measurements of $\nu(N_2)$ in $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ and in the bridging dinitrogen species were determined and are discussed.

Introduction

The reactions of the complex, *trans*-$[Re(C_6H_5(CH_3)_2P)_4(N_2)Cl]$, with a variety of acceptor molecules has been shown by Chatt and coworkers[1,2] to result in formation of adducts which appear to have a dinitrogen bridging group between the rhenium and the acceptor atom. These adducts have $\nu(N_2)$ bands occurring significantly lower than that in $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$.

Since interactions of this type are thought to be very important in the reduction of the dinitrogen ligand[2-4] an infrared study of the nature of the interaction in solution has been undertaken. Chatt and coworkers[1] have reported the formation of a green complex (of unknown ratio) resulting from $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ and *trans*-$[Re(O)[P(C_6H_5)_3]_2Cl_3]$ with $\nu(N_2)$ at 1842 cm^{-1}(Nujol mull). Because of the stability of $Re(O)[P(C_6H_5)_3]_2Cl_3$ towards oxygen as compared with the other Lewis acid addenda reported, the interaction between $Re(O)[P(C_6H_5)_3]_2Cl_3$ and $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ was investigated in chloroform solution. In addition, the interaction in solution between $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ and the Re^V derivative, $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ was studied.

Experimental Section

Preparation and Purification of Materials. Chlorodinitrogen-tetrakis[dimethyl(phenyl)phosphine]rhenium(I), $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$, was prepared and purified by the method of Chatt aend co-workers.[5] *trans*-Oxotrichlorobistriphenylphosphinerhenium(V), $Re(O)[P(C_5H_5)_3]_2Cl_3$, and Oxomethoxydichlorobistriphenylphosphosphinerhenium(V), $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$, were prepared and purified by the procedure of Chatt and Rowe.[6] Spectrograde chloroform was employed without further purification. All reactions were carried out under a dry nitrogen atmosphere.

Infrared Measurements. Infrared spectra were measured on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. Spectral samples were prepared by weighing out the solid materials on a Cahn Electrobalance to ± 0.01 mg. The Beer's Law plot obtained for $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ was linear over the involved concentration range. Spectra were observed in chloroform solution using sealed 0.1 cm NaCl cells for both sample and reference. The cells were calibrated by the interference fringes method. The spectrophotometer was calibrated in the region above 2000 cm^{-1} against the spectrum of carbon monoxide and below 2000 cm^{-1} against the spectrum of water vapor.

The areas under the band envelopes employed in integrated intensity determinations were determined with a planimeter.

Microanalyses. Carbon, hydrogen, and nitrogen analyses on the complexes studied, as well as, osmo-

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(1) J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 955 (1970).

(2) J. Chatt, J. R. Dilworth, R. L. Richards, and J. R. Sanders, *Nature, 224,* 1201 (1969)

(3) M. E. Vol'pin, V. S. Lenenko, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim. *1971,* (2), 463.

(4) Yu G. Borodko, M. O. Broitman, L. M. Kachapina, A. E. Shilov, and L. Yu, Ukhin. *Chem. Commun.*, 1185 (1971).

(5) J. Chatt, J. R. Dilworth, and G. L. Leigh, *Chem. Commun.*, 687 (1969).

(6) J Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

metric molecular-weight measurements in chloroform, were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York. *Anal.* Calcd. for $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$: %C, 48.0; %H, 5.5; %N, 3.5. Found %C, 48.20; %H, 5.63; %N, 3.86. Calcd for $Re(O)[P(C_6H_5)_3]_2Cl_3$: %C, 51.9; %H, 3.6. Found %C, 51.82; %H, 3.75. Calcd. for $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$: %C, 53.6; %H, 4.0. Found %C, 53.74, %H, 4.14.

Results

Figure 1 depicts the infrared spectra of various mixtures of $ReC_6H_5(CH_3)_2P)_4(N_2)Cl$ and $Re(O)[P(C_5H_5)_3]_2Cl_3$ in chloroform solution. The spectra consists of a band at 1921 cm^{-1} corresponding to $\nu(N_2)$ in the uncomplexed rhenium dinitrogen species and bands at 1843 and 1820 cm^{-1} assigned to $\nu(N_2)$ resulting from adduct formation at the terminal nitrogen.[7] Figure 2 shows the linearity of a plot of the absorbance of the band at 1820 cm^{-1} in the adduct *versus* the absorbance of the band at 1921 cm^{-1} in $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$. An equilibrium in which a binuclear bridging dinitrogen species is present in solution is proposed (eq. 1).[8]

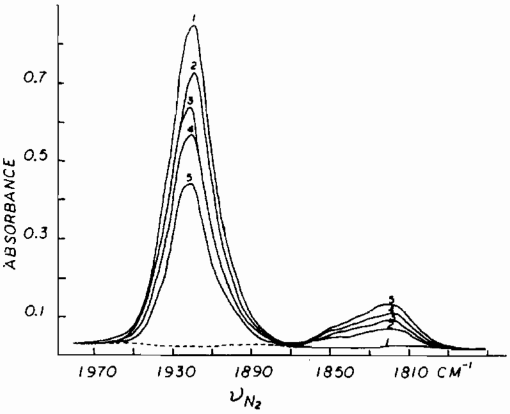

Figure 1. Infrared spectra of $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)[P(C_5H_5)_3]_2Cl_3$ in chloroform in a 1 mm cell. The numbers correspond to $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)[P(C_6H_5)_3]_2Cl_3$ molar concentrations, respectively: 1) 5.92×10^{-3} and 0.0000; 2) 5.93×10^{-3} adn 2.90×10^{-3}; 3) 5.91×10^{-3} and 5.11×10^{-3}; 4) 5.96×10^{-3} and 7.23×10^{-3}; 5) 5.88×10^{-3} and 11.2×10^{-3}. The dashed line corresponds to $Re(O)[P(C_6H_5)_3]_2Cl_3$, $11.2\times10^{-3}M$ in $CHCl_3$. Similar spectra were observed for a constant $Re(O)[P(C_6H_5)_3]_2Cl_3$ concentration with varying $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ concentrations.

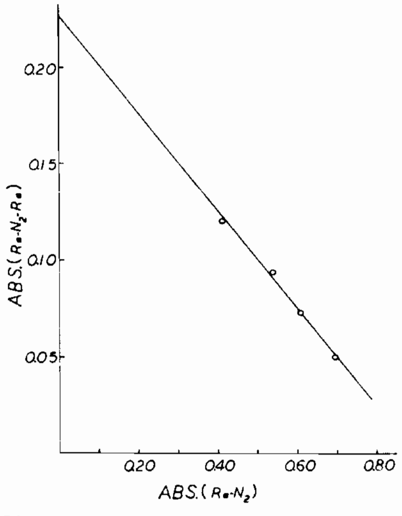

Figure 2. Plot of the increase in absorbance of $\nu(N_2)$ in the bridging binuclear species, $\{[(C_6H_5)(CH_3)_2P]_4ClReN_2Re(O)P(C_6H_5)_3Cl_3]\}$, versus the simultaneous decrease in absorbance of the $\nu(N_2)$ in $Re\ [C_5H_5)(CH_3)_2P]_4(N_2)Cl$.

$$Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl+Re(O)Cl_3[P(C_6H_5)_3]_2 \leftrightarrows \quad (1)$$
$$[(C_6H_5)(CH_3)_2]_4(Cl)Re{-}N{\equiv}N{-}Re(O)Cl_3P(C_6H_5)_3+P(C_6H_5)_3$$

The following evidence supports this:

(i) Free $P(C_5H_5)_3$ is detected in the solution infrared spectrum when the two rhenium complexes are mixed.[9] On addition of excess $P(C_6H_5)_3$ to a mixture of the rhenium complexes the infrared spectrum of $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ is *quantitatively* restored.

(ii) Average molecular weight measurements (osmometric in chloroform) of several mixtures of the two rhenium complexes in varying ratios gave an average molecular weight value of 800±30 in all cases (the average calculated mole wt. on either side of the equilibrium is 818). This is consistent with the proposed equilibrium for the bridging dinitrogen species and is incompatiable with a bridging species containing a five- or seven-coordinate Re^V species.

(iii) The calculated equilibrium constant for this process, as prosposed in equation 1, for six different mixtures of the two rhenium complexes gave an ave-

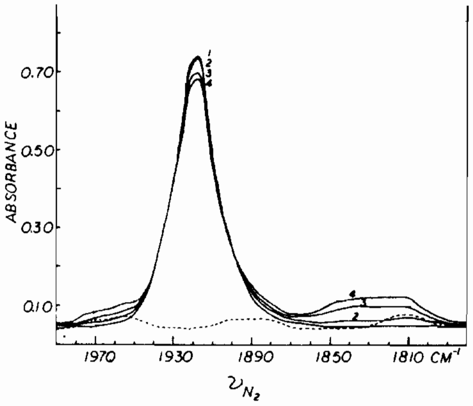

Figure 3. Infrared spectra of $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ in chloroform in a 1 mm cell. The numbers correspond to $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ molar concentrations, respectively: 1) 4.40×10^{-3} and 0.000; 2) 4.50×10^{-3} and 5.21×10^{-3}; 3) 4.50×10^{-3} and 12.8×10^{-3}; 4) 4.43×10^{-3} and 18.5×10^{-3}. The dashed line corresponds to $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$, $17.1\times13^{-3}M$ in chloroform.

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(7) The two $\nu(N_2)$ bands may result from the presence of two complexes containing a *cis* or *trans* $P(C_6H_5)_3$ group in the Re^V moiety relative to the dinitrogen.

(8) An analogous process between $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ and $CrCl_3(thf)_3$ resulting in 100% adduct formation has been reported by J. Chatt, R. C. Fay, and R. L. Richards, J. Chem. Soc. (A), 702 (1971).

(9) No free phosphine in detected under similar conditions for $Re(O)[(C_6H_5)_3P]_2Cl_3$ alone in chloroform solution.

rage K_{eq} value of 0.28±0.03 at 27°C. These were computed from known concentrations of Re^I and Re^V samples before mixing and the quantity of Re^I dinitrogen species present ofter equilibrium is attained, as determined from the $\nu(N_2)$ absorption.

In order to further study this equilibrium process the reaction was carried out with an additional Re^V complex, $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$. Figure 3 depicts the infrared spectra of sevarl mixture of $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ (at constant initial concentrations) and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ (initial concentrations varied) in chloroform. The spectra consist of two bands at 1921 and 1837 cm^{-1} which are assigned to $\nu(N_2)$ in the uncomplexed rhenium dinitrogen species and the rhenium dinitrogen – Re^V adduct, respectively. Figure4 illustrates the effect of maintaining a constant concentration of Re(O) $(OCH_3)[P(C_6H_5)_3]_2Cl_2$ while varying the $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ concentration. From an analysis of these spectral results it is possible to conclude that a similar equilibrium process is taking place for the methoxy-bubstituted rhenium(V) derivative as that described in equation (1). The principal difference being that in this case the equilibrium lies further to the left; i.e., $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ is less effective than $Re(O)[P(C_6H_5)_3]_2Cl_3$ in adduct formation with $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$. The calculated equilibrium constant for several mixtures of the two rhenium complexes gave an average K_{eq} value of 0.004±0.002 at 27°C[10].

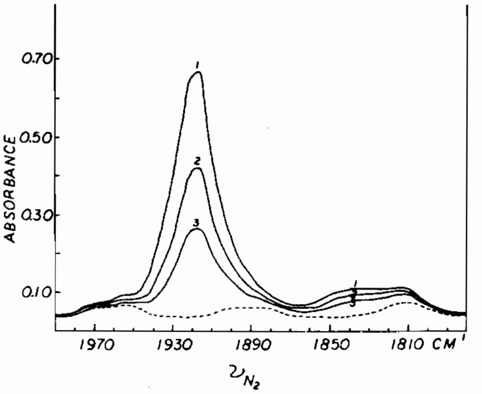

Figure 4. Infrared spectra of $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_3$ in chloroform in a 1 mm cell. The numbers correspond to $Re[(C_6H_5)(CH_3)_2P]_4(N_2)Cl$ and $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$ molar concentrations, respectively: 1) 4.43×10^{-3} and 18.5×10^{-3}; 2) 1.73×10^{-3} and 18.4×10^{-3}; 3) 2.75×10^{-3} and 18.5×10^{-3}. The dashed line corresponds to $Re(O)(OCH_3)[P(C_6H_5)_3]_2Cl_2$, $17.1\times10^{-3}M$ in chloroform.

Since the interaction between the methoxy derivative of rhenium(V) and $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$ is weak, complete analysis, including molecular weight measurements, of adduct formation was not possible However, the fact that the interaction is significantly weaker in the methoxy derivative of rhenium(V) as compared with its chloro- analog strongly illustrates the sensitivity of the interaction of the rhenium(I) dinitrogen complex to the Lewis acid character of the rhenium(V) species. The methoxy group is electron donating relative to the chloride ligand, therefore, $-Re(O)(OCH_3)[P(C_6H_5)_3]Cl_2$ is excepted to be a poorer Lewis acid than $-Re(O)[P(C_6H_5)_3]Cl_3$.

The bonding in the $[(C_6H_5(CH_3)_2P)_4ClReN_2CrCl_3(THF)_2]$ species has been discussed in detail based on electronic spectral analysis in terms of a qualitative molecular orbital model.[8] In order to further understand this type of interaction infrared intensity measurements were performed on these $Re^I–N_2–Re^V$ complexes. The absolute infrared intensity of $\nu(N_2)$ in the binuclear bridging species $[(C_6H_5(CH_3)_2P)_4ClReN_2Re(O)P(C_6H_5)_3Cl_3]$ was found to be 4.81×10^4 M^{-1} cm^{-2} (extrapolated to 100% adduct formation, see Figure 5) compared to 10.8×10^4 M^{-1} cm^{-2} for the uncomplexed $Re[C_6H_5(CH_3)_2P]_4(N_2)Cl$ species.[11] Although, the intensity value in the $[(C_6H_5(CH_3)_2P)_4ClReN_2Re(O)(OCH_3)[P(C_6H_5)_3]Cl_2]$ adduct is less accurately measurable, a value of 11 ± 10^4 M^{-1} $–cm^{-2}$ was estimated for this species.

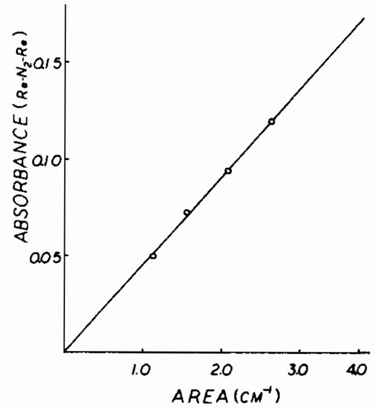

Figure 5. Plot of the area of the $\nu(N_2)$ in the bridging binuclear species, $\{[(C_6H_5)(CH_3)_2P]_4ClReN_2Re(O)P(C_6H_6)_3Cl_3]\}$, versus the absorbance of this vibration.

It is expected that Lewis acid adduct formation with the terminal nitrogen in Re–N≡N would result in an increase in the dipole moment derivative as the N_2 stretches, and therefore, an increase in the absolute intensity.[12] Shilov and coworkers[4] have attributed a sizable decrease in intensity of $\nu(N_2)$ in a binuclear dinitrogen bridging species containing non-equivalent iron(I) and iron(II) moieties as compared with mononuclear $Fe-Ne_2$ complexes to considerable electron transfer from *both* of the iron atoms to the nitrogen molecule. A similar explanation would explain the lower infrared intensity observed in the $[(C_6H_5(CH_3)_2P)_4ClReN_2Re(O)P(C_6H_5)_3Cl_3]$ species *versus* that in

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(10) Attempts at measuring other Re^V species interactions with $Re(C_6H_5(CH_3)_2P)_4(N_2)Cl$, such as $Re(O)[P(C_6H_5)_3]_2(SCN)_3$, failed due to either a lack of sufficient interaction or to solubility problems.

(11) D. J. Darensbourg, *Inorg. Chem.*, *11*, 1436 (1972).

(12) The infrared intensity of the $\nu(N_2)$ is a measure of the extent of π-electronic charge transfer from the metal to the N_2 as the N_2 stretches.11,13,14 Qualitatively, the intensity of $\nu(N_2)$ in the bridging dinuclear species between Re^I and Cr^{III} has increased over that in the Re^IN_2 species[8] (personal communications with Professor R. C. Fay).

(13) D. J. Darensbourg and C. L. Hyde, *Inorg. Chem.*, *10*, 431 (1971)

(14) D. J. Darensbourg, *ibid.*, *10*, 2399 (1971).

$[C_6H_5(CH_3)_2P]_4Re(N_2)Cl$. However, this would imply that the Re^V species is behaving as a π donor ligand as well as a σ acceptor. This is a rather tenuous conclusion and indeed a qualitative extension of infrared intensity arguments which may be theoretically unsound. A more definitive conclusion will have to await a better understanding of infrared intensities in unsymmetrical bridging dinitrogen or related carbon monoxide species.

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