

RHENIUM(I) COMPLEXES OF (2-CYANOETHYL)DIPHENYLPHOSPHINE

B. N. STORHOFF

Department of Chemistry, Ball State University, Muncie, Indiana 47306 (U.S.A.)

(Received April 7th, 1972)

SUMMARY

Rhenium pentacarbonyl halides react with (2-cyanoethyl)diphenylphosphine (L) to yield complexes of the stoichiometry $[\text{Re}(\text{CO})_3\text{LX}]_n$. The infrared spectra of the complexes are consistent with structures containing terminal halogens and bridging L groups. Molecular weight studies indicate that n is two for solutions of $10^{-3} M$. The nitrile portion of the ligand is readily displaced by σ donor ligands to yield complexes in which L functions as a monodentate phosphine.

INTRODUCTION

Transition metal complexes containing bidentate phosphine ligands such as $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NC}^1$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SCH}_3^2$, and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CH}_2^3$ have been reported. The analogous phosphine-nitrile, (2-cyanoethyl)diphenylphosphine (L), has been characterized, but little is known about its ability to coordinate as either a monodentate or bidentate ligand⁴.

This study was initiated to investigate the ability of L to function as a bidentate ligand. For L to function as a chelating bidentate ligand the phosphorus lone pair and nitrile triple bond would be required to coordinate simultaneously because of the linear arrangement of the CN group. Alternatively, L could function as a bridging bidentate ligand utilizing the phosphorus and nitrogen lone pairs. Rhenium(I) carbonyl complexes were chosen as reactants because phosphine⁵ and nitrile^{6,7} ligands readily replace two carbonyl groups and form stable complexes.

EXPERIMENTAL

(2-Cyanoethyl)diphenylphosphine was prepared according to the published procedure⁴. Bromo- and chloropentacarbonylrhenium(I) were prepared from $\text{Re}_2(\text{CO})_{10}$ by the procedures described for the analogous manganese complexes⁸. The solvents were stored over type 4A molecular sieves. All reactions were carried out under a positive pressure of dry nitrogen.

Infrared absorption spectra in the $4000\text{--}650\text{ cm}^{-1}$ range were recorded on a Beckman IR-10 spectrophotometer. The low energy infrared data, $400\text{--}100\text{ cm}^{-1}$, were recorded on a Beckman IR-12 spectrophotometer at the University of Iowa. Raman spectra were recorded at Purdue University by Professor R. S. Tobias.

TABLE 1

MOLECULAR WEIGHT AND ANALYTICAL DATA

| | Analysis found (calcd.) (%) | | | | Mol.wt. ^a found (calcd.) |
|--|-----------------------------|----------------|----------------|------------------|--|
| | C | H | N | X | |
| [Re(CO) ₃ LBr] ₂ | 37.01 (36.68) | 2.17 (2.39) | 2.34 (2.38) | 13.63 (13.56) | 1170 ^b (1179) |
| [Re(CO) ₃ LCl] ₂ | 39.43 (39.67) | 2.66 (2.59) | 2.70 (2.57) | | 1145 ^b (1090) |
| Re(CO) ₃ L(C ₅ H ₅ N)Br | 41.11 (41.32) | 2.84 (2.86) | 4.02 (4.19) | | 744 ^c (669) |
| Re(CO) ₃ L(C ₅ H ₅ N)Cl | 44.32 (44.27) | 3.10 (3.07) | 4.76 (4.49) | | |
| Re(CO) ₃ L(PPh ₃)Br | 50.58 (50.77) | 3.41 (3.43) | | 9.47 (9.38) | |
| Re(CO) ₃ L ₂ Br | 47.60 (47.83) | 3.37 (3.40) | 3.70 (3.38) | | |
| Re(CO) ₄ LBr | 37.04 (36.96) | 2.39 (2.29) | 2.42 (2.29) | 12.76 (12.94) | |

^a The value of 1170 is the mean of 6 determinations with a standard deviation of 42. The values of 1145 and 744 were obtained from single samples. ^b Measured in dichloromethane. ^c Measured in benzene.

The molecular weights were measured with a Hitachi-Perkin-Elmer model 115 molecular weight apparatus in either dichloromethane or benzene. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, and the data are summarized in Table 1.

Preparation of Re₂(CO)₆[Ph₂P(CH₂)₂CN]₂X₂ (X = Cl, Br)

Re(CO)₅X (0.82 mmole), Ph₂P(CH₂)₂CN (0.20 g, 0.84 mmole) and 20 ml of benzene were refluxed for 4 h. During the reaction period the colorless products precipitated. After cooling, the precipitates were collected on a filter, washed with 10 ml of hot benzene and dried to yield 90–95% of product. The colorless solids were crystallized from a mixture of dichloromethane and hexane.

Preparation of Re(CO)₃[Ph₂P(CH₂)₂CN](C₅H₅N)X (X = Cl, Br)

Re₂(CO)₆[Ph₂P(CH₂)₂CN]₂X₂ (0.43 mmole) and 0.50 ml of pyridine were stirred in 25 ml of dichloromethane for 6 h. As the reactions proceeded the starting material dissolved leaving colorless solutions. The solutions were evaporated to dryness, yielding colorless solids which were crystallized from dichloromethane-hexane. The yields were quantitative except for mechanical losses.

Preparation of Re(CO)₃[Ph₂P(CH₂)₂CN][PPh₃]Br and Re(CO)₃[Ph₂P(CH₂)₂CN]₂-Br

These complexes were prepared and isolated by the procedure described for Re(CO)₃[Ph₂P(CH₂)₂CN](C₅H₅N)X. In each case an excess of ligand was used.

Preparation of Re(CO)₄[Ph₂P(CH₂)₂CN]Br

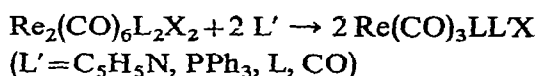
Re₂(CO)₆[Ph₂P(CH₂)₂CN]₂Br₂ (0.130 g, 0.110 mmole) was refluxed for two

hours in 30 ml of benzene while carbon monoxide was bubbled through the mixture. As the reaction proceeded the insoluble starting material dissolved. The colorless solid crystallized from dichloromethane/hexane to yield 0.124 g (91%) of product.

RESULTS AND DISCUSSION

Halopentacarbonylrhenium(I) complexes (Cl, Br) react with one mole equivalent of (2-cyanoethyl)diphenylphosphine (L) to yield colorless products of the stoichiometry $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$. These products are stable showing no decomposition when stored in air for several months. The stoichiometries have been confirmed by elemental analyses and molecular weight measurements as indicated in Table 1. The complexes are only slightly soluble in chlorinated solvents and insoluble in water. The substitution pattern is the usual one in which the halogen is retained in the inner coordination sphere. The molecular weight data were recorded using dilute solutions with concentrations between 0.084 and 0.17 weight percent, 6.3×10^{-4} and 1.3×10^{-3} molal respectively. Unfortunately, thorough molecular weight studies were difficult because the complexes are only moderately soluble in noncoordinating solvents and they react with coordinating solvents (*vide infra*) to form monomeric complexes.

The dimeric complexes readily react with donor solvents and σ donor ligands to yield monomeric complexes of the well known stoichiometry, $\text{Re}(\text{CO})_3\text{LL}'\text{X}$. Previous studies of organonitrile complexes of rhenium(I) have indicated that the



coordinated nitriles can be replaced by σ donor ligands⁶. Thus the facile reactions observed for $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$ with phosphines, pyridine and carbon monoxide suggest that these ligands have replaced coordinated nitrile groups.

Infrared spectra and structures

The infrared absorptions in the carbonyl and nitrile regions are listed in Table 2. Both the dimeric complexes $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$ and the monomeric complexes $\text{Re}(\text{CO})_3\text{LL}'\text{X}$ ($\text{L}' = \text{C}_5\text{H}_5\text{N}, \text{PPh}_3, \text{L}$) exhibit three intense $\nu(\text{CO})$ bands. The observed pattern is identical to that observed for complexes in which the CO groups are in a

TABLE 2

INFRARED AND RAMAN DATA (cm^{-1})

| | $\nu(\text{CO})^a$ IR | $\nu(\text{CN})^b$ IR | $\nu(\text{CN})^c$ Raman | $\nu(\text{ReX})^d$ IR |
|---|--------------------------------|--------------------------|-----------------------------|---------------------------|
| $[\text{Re}(\text{CO})_3\text{LBr}]_2$ | 2040 s, 1980 s, 1940 s | 2295 w | 2293 s | 198 s |
| $[\text{Re}(\text{CO})_3\text{LCl}]_2$ | 2040 s, 1980 s, 1940 s | 2295 w | 2296 s | 288 s |
| $\text{Re}(\text{CO})_3\text{L}(\text{C}_5\text{H}_5\text{N})\text{Br}$ | 2030 s, 1965 s, 1910 s | 2230 m, 2250 m | | |
| $\text{Re}(\text{CO})_3\text{LPPh}_3\text{Br}$ | 2030 s, 1975 s, 1925 s | 2225 m, 2250 m | | |
| $\text{Re}(\text{CO})_3\text{L}_2\text{Br}$ | 2025 s, 1975 s, 1930 s | 2220 m, 2240 m | | |
| $\text{Re}(\text{CO})_4\text{LBr}$ | 2105 s, 2020 s, 2000 s, 1975 m | 2235 m, 2255 m | | |
| $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CN}$ | | 2230 m, 2250 m | | |

^a CHCl_3 solution. ^b KBr disc. ^c Solid sample. ^d Nujol mull.

fac arrangement⁹. The tetracarbonyl complex $\text{Re}(\text{CO})_4\text{LBr}$ exhibits four $\nu(\text{CO})$ bands which is consistent with *cis* substitution.

For the dimeric complexes very weak $\nu(\text{CN})$ IR bands are observed at 2295 cm^{-1} , increases of nearly 50 cm^{-1} over that observed for the uncomplexed ligand. These bands are very intense in the Raman spectra. The IR spectra of organonitrile complexes of rhenium(I) generally exhibit $\nu(\text{CN})$ bands of sufficient intensity to be readily observed⁶. Very weak bands as observed for the dimeric complexes are not without precedence, however. For example, the infrared spectrum of $[\text{Re}(\text{CO})_3(\text{NCCH}_2\text{CH}_2\text{CN})\text{Cl}]_2$ exhibits a very weak band at 2302 cm^{-1} which is assigned to a *N*-bonded nitrile group¹⁰. This band is very intense in the Raman spectrum.

Increases in the nitrile stretching frequencies of similar magnitudes to those observed for $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$ are well documented and considered characteristic of coordination involving the nitrogen lone pair electrons^{11,12}. In contrast, coordination involving the $(\text{CN})\pi$ electrons is expected to shift the $\nu(\text{CN})$ bands to lower frequencies as observed for diethylaminoacetonitrile complexes of metal carbonyls¹³. Accordingly, the infrared data suggest that the nitrile portion of L is coordinated through the nitrogen lone pair electrons. Since the linear hybridization of the CN group prevents chelation, L must function as a bridging ligand in the dimeric complexes.

The monomeric complexes $\text{Re}(\text{CO})_3\text{LL}'\text{X}$ ($\text{L}' = \text{C}_5\text{H}_5\text{N}$, PPh_3 , L, CO) exhibit two $\nu(\text{CN})$ bands at essentially the same frequencies as those observed for the uncomplexed ligand. These data indicate that the nitrile portion of the ligand is not coordinated and that L is functioning as a monodentate phosphine. A study of $\text{Ni}_4(\text{CO})_6[\text{P}(\text{C}_2\text{H}_4\text{CN})_3]_4$ in which the nitrile groups are uncoordinated also indicated that the $\nu(\text{CN})$ did not shift upon coordination through only the phosphorus^{14,15}.

The low energy infrared spectra of $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$ exhibit only one metal-halogen band which is consistent with structures containing terminal halogens. The $\nu(\text{ReCl})$ appears at 288 cm^{-1} while the $\nu(\text{ReBr})$ appears at 198 cm^{-1} . The observed $\nu(\text{ReX})$ bands are of comparable frequencies to those reported for terminal halogens *trans* to a CO group¹⁶⁻¹⁸.

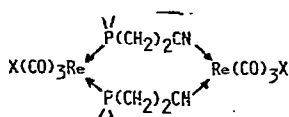
Organonitrile complexes such as $\text{Re}_2(\text{CO})_6(\text{MeCN})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been reported⁷ which are of identical stoichiometry to the complexes reported here. These dimeric complexes are halogen bridged and they display two strong $\nu(\text{ReX})$ bands in their infrared spectra.

The spectroscopic and molecular weight evidence suggests that $\text{Re}_2(\text{CO})_6\text{L}_2\text{X}_2$ may be formulated as dimeric complexes containing bridging L groups. The appearance of three strong $\nu(\text{CO})$ bands is in accord with *fac* arrangements of the CO groups on each metal center assuming that coupling between the two halves of the molecule is negligible. Similarly the spectroscopic evidence confirms that the monomeric complexes are of the structure *fac*- $\text{Re}(\text{CO})_3\text{LL}'\text{X}$ in which L functions as a monodentate phosphine.

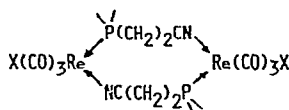
The proposed bridging function of L is similar to the bridging properties of R_2PCN in $(\text{R}_2\text{PCN})_2\text{M}_2(\text{CO})_8$ ($\text{M} = \text{Cr}, \text{Mo}$)^{19,20}. The isocyanide which is isomeric with L, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NC}$, is also believed to function as a bridging ligand and form complexes of the type $\text{Cr}_3(\text{CO})_{12}\text{L}'_4$ ¹.

The bridging unit gives rise to two possible isomers. The more symmetrical

isomer (B) is favored because bridge splitting reactions yield only one product Re(CO)₃LL'X. Assuming no rearrangement, (A) would be expected to yield both Re(CO)₃L₂X and Re(CO)₃L'₂X.



(A)



(B)

ACKNOWLEDGEMENTS

The author thanks Professor J. R. Doyle and Professor R. S. Tobias for the low energy infrared and Raman data. This research was supported in part by a grant from Ball State University.

REFERENCES

- 1 R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93 (1971) 564.
- 2 E. P. Ross and G. R. Dobson, *J. Inorg. Nucl. Chem.*, 30 (1968) 2363.
- 3 G. E. Hartwell and P. W. Clark, *J. Chem. Soc. D*, (1970) 1115.
- 4 F. G. Mann and I. T. Millar, *J. Chem. Soc.*, (1952) 4453.
- 5 M. Freni, V. Valenti and D. Giusto, *J. Inorg. Nucl. Chem.*, 27 (1965) 2635.
- 6 B. N. Storhoff, *Dissertation Abstr.*, 30B (1969) 549.
- 7 J. G. Dunn and D. A. Edwards, *J. Organometal. Chem.*, 27 (1971) 73.
- 8 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, (1959) 1501.
- 9 R. J. Angelici, F. Basolo and A. J. Poe, *J. Amer. Chem. Soc.*, 85 (1963) 2215.
- 10 J. G. Dunn and D. A. Edwards, *J. Chem. Soc. D*, (1971) 482.
- 11 K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, 88 (1966) 919.
- 12 R. A. Walton, *Quart. Rev.*, 19 (1965) 126.
- 13 S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, 3 (1969) 249.
- 14 M. J. Bennett, F. A. Cotton and B. H. C. Winquist, *J. Amer. Chem. Soc.*, 89 (1967) 5366.
- 15 L. S. Meriwether, E. C. Colthup, M. L. Fiene and F. A. Cotton, *J. Inorg. Nucl. Chem.*, 11 (1959) 181.
- 16 M. J. Hawkes and A. P. Ginsberg, *Inorg. Chem.*, 8 (1969) 2189.
- 17 E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, 47 (1969) 4627.
- 18 M. F. Faroni and K. F. Kraus, *Inorg. Chem.*, 9 (1970) 1700.
- 19 C. E. Jones and K. J. Coskran, *Inorg. Chem.*, 10 (1971) 1664.
- 20 J. F. Nixon and J. R. Swain, *J. Organometal. Chem.*, 21 (1970) C13.

J. Organometal. Chem., 43 (1972)