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Cyclooctene and β-Diketonato Derivatives of Carbonylnitrosyl Complexes of Rhenium

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The reaction of $[Re(CO)_2(NO)Cl_2]_2$ (I) with cyclooctene gives the chloro-bridged olefin derivative $[Re(CO)(NO)(\text{cyclooctene})Cl_2]_2$ (II). The chloride bridge in II can be split by monodentate ligands L to give monomeric complexes of formula $Re(CO)(NO)Cl_2L_2$ (III) with displacement of the coordinated olefin. The reaction of I with β-diketones of the type $RCOCH_2COR$ ($R = CH_3$, CF_3, C_6H_5) affords complexes of formula $Re(CO)_2(NO)ACl$ (AH = β-diketone).

Introduction

We have recently described the synthesis and characterization of new halide-bridged dimeric dicarbonylnitrosylrhenium halides of the formula $[Re(CO)_2(NO)X_2]_2$ (X = Cl, Br, I) and of their monomeric monosubstituted derivatives, $Re(CO)_2(NO)X_2L$, where L is a neutral monodentate ligand having N, P, O, or S as donor atoms.[1]

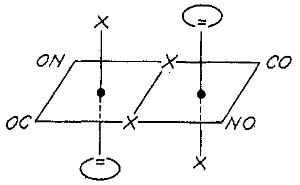
We shall now report the preparation of the chloride-bridged dimeric π-olefin complex $[Re(CO)(NO)(C_8H_{14})Cl_2]_2$ (C_8H_{14} = cyclooctene) and of its substituted derivatives with neutral monodentate ligands. We shall also describe the reaction of $[Re(CO)_2(NO)Cl_2]_2$ with β-diketones which gives novel complexes of the formula $Re(CO)_2(NO)ClA$ (AH = acetylacetone, dibenzoylmethane, or hexafluoroacetylacetone).

Results and Discussion

(A) Reaction of $[Re(CO)_2(NO)Cl_2]_2$ with Cyclooctene.—Unlike strong σ-donor ligands, π-donor ligands such as cyclooctene react with $[Re(CO)_2(NO)Cl_2]_2$ (I) to give a compound (II) which retains the halide-bridged dimeric configuration according to the reaction

$$\underset{\text{I}}{[Re(CO)_2(NO)Cl_2]_2} + 2C_8H_{14} \longrightarrow \underset{\text{II}}{[Re(CO)(NO)(C_8H_{14})Cl_2]_2} + 2CO \quad (1)$$

The cream yellow product II is air stable, diamagnetic in the solid, nonconducting in nitrobenzene, soluble in chlorinated solvents and acetone, and insoluble in aliphatic hydrocarbons. Its dimeric structure is indicated by osmometric molecular weight determinations (Table I). Infrared bands in the Re–Cl stretching region (Table II) indicate the presence of a chloro-bridged structure. In fact, the three bands that appear in this region are very close to those of the previously reported chloro-bridged parent compound I in both intensity and frequency.[1] Based on these data and also on infrared spectral features in the CO and NO stretching regions (*i.e.*, one single ν_{CO} and one single ν_{NO} absorption), the most probable structure for the product II should be



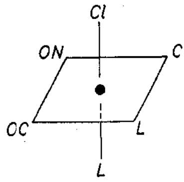
The chloride bridge in II can be easily split by reaction with neutral monodentate ligands (L) bearing N, P, or As as donor atoms. Under the reaction conditions that we employed, substitution of the coordinated olefin by 1 further mol of entering ligand takes place, whereby the monomeric disubstituted derivatives $Re(CO)(NO)Cl_2L_2$ are obtained. Infrared spectra of the reaction mixtures recorded at various time intervals clearly indicate that the first reaction product, which cannot be isolated, still retains the coordinated olefin. This intermediate then undergoes a subsequent replacement of the olefin by entering ligand, according to the reaction sequence

$$[Re(CO)(NO)(C_8H_{14})Cl_2]_2 + 2L \longrightarrow 2Re(CO)(NO)(C_8H_{14})Cl_2L \xrightarrow[-C_8H_{14}]{+L} \underset{\text{III}}{Re(CO)(NO)Cl_2L_2} \quad (2)$$

where L = pyridine, 2-chloropyridine, triphenylarsine, or triphenyl phosphite.

It is noteworthy that the disubstituted derivatives III cannot be prepared by direct reaction of $[Re(CO)_2(NO)Cl_2]_2$ with ligands L, even under drastic conditions and with an excess of ligand. Analytical data and relevant infrared bands for these complexes are reported in Tables I and II.

Complexes III are monomeric, as indicated by osmometric molecular weight measurements. They are diamagnetic in the solid, nonconducting in nitrobenzene, soluble in chlorinated solvents and acetone, and insoluble in aliphatic hydrocarbons. Based on infrared spectra we suggest the structure



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(1) F. Zingales, A. Trovati, F. Cariati, and P. Uguagliati, *Inorg. Chem.*, **10**, 507 (1971); F. Zingales, A. Trovati and P. Uguagliati, *ibid.*, **10**, 510 (1971).

TABLE I

			Mol wt[a]		Analyses, %									
					C		H		N		O		Halogen	
Complex	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Re(CO)(NO)(C_8H_{14})Cl_2]_2$	Cream yellow	>300	851	862	25.41	25.25	3.32	3.29	3.29	3.16	7.52	7.88	16.67	15.93
$Re(CO)(NO)(py)_2Cl_2$	Orange-yellow	290	473	490	27.91	28.02	2.13	2.02	8.88	8.94	...	...	...	...
$Re(CO)(NO)(2\text{-}Cl(py))_2Cl_2$	Green	235	542	553	24.36	24.36	1.49	1.75	7.75	7.57	...	...	...	...
$Re(CO)(NO)(As(C_6H_5)_3)_2Cl_2$	Orange-yellow	270	928	940	47.90	47.62	3.27	3.15	1.51	1.61	3.45	3.52	7.64	7.15
$Re(CO)(NO)(P(OC_6H_5)_3)_2Cl_2$	White	132	936	905	47.49	47.72	3.24	3.34	1.50	1.58	13.68	13.73	...	...

[a] Determined in chloroform solution using a Mechrolab Model 301 A osmometer.

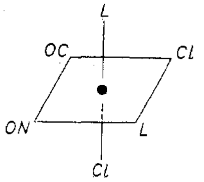
TABLE II

C–O, N–O, AND Re–Cl STRETCHING FREQUENCIES (cm^{-1})[a]

Complex[c]	C–O	N–O	Re–Cl[b]
$[Re(CO)_2(NO)Cl_2]_2$	2106 vs 2047 vs	1803 vs	331 s 290 s 252 m
$[Re(CO)(NO)(C_8H_{14})Cl_2]_2$	2058 vs	1770 vs	326 s 283 s 250 m
$Re(CO)(NO)(py)_2Cl_2$	2008 vs	1722 vs	309 s 289 s
$Re(CO)(NO)(2\text{-}Cl(py))_2Cl_2$	2000 vs	1738 vs	311 s 277 s
$Re(CO)(NO)(As(C_6H_5)_3)_2Cl_2$	2000 vs	1733 vs	327 s 288 s
$Re(CO)(NO)(P(OC_6H_5)_3)_2Cl_2$	2034	1739 vs	318 s 278 s

[a] All spectra recorded using a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium. [b] Nujol mull between CsI disks. [c] In CCl_4 solution.[1]

as the most likely one for these complexes. In fact, the two almost equally intense bands observed in the Re–Cl stretching region indicate a cis configuration for the two chloride ligands. Further, it is likely that one L molecule is in the trans position to the coordinated NO group, as in the previously described monosubstituted derivatives $Re(CO)_2(NO)X_2L$.[1] However, the other possible structure, namely



cannot be ruled out.

TABLE III

			Mol wt[a]		Analyses, %							
					C		H		N		O	
Complex	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Re(CO)_2(NO)(C_5H_7O_2)Cl$	Lemon yellow	102	407	403	20.67	20.78	1.74	1.76	3.44	3.46	19.67	19.85
$Re(CO)_2(NO)(C_{15}H_{11}O_2)Cl$	Yellow	116	531	550	38.46	38.92	2.09	2.15	2.64	2.58	...	...
$Re(CO)_2(NO)(C_5HF_6O_2)Cl$	Green	82	515	521	16.33	16.74	0.20	0.47	2.72	2.71	...	...

[a] Determined in chloroform solution using a Mechrolab Model 301 A osmometer.

TABLE IV

$C{\equiv}O$, $C\overset{...}{-}O$, N—O, AND Re—Cl STRETCHING FREQUENCIES (cm^{-1})[a]

Complex	$C{\equiv}O$	N—O	$C\overset{...}{-}O$	Re—Cl[b]
$Re(CO)_2(NO)(C_5H_7O_2)Cl$	2098 vs 2025 vs	1769 vs	1566 m 1524 s	316 s
$Re(CO)_2(NO)(C_{15}H_{11}O_2)Cl$	2098 vs 2025 vs	1769 vs	1587 w 1524 s	316 s
$Re(CO)_2(NO)(C_5HF_6O_2)Cl$	2114 vs 2046 vs	1789 vs	1632 m 1611 s	

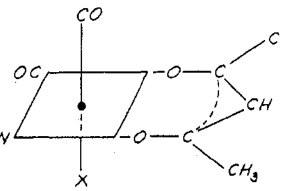
[a] All spectra recorded using a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium; w, weak. [b] Nujol mull between CsI disks.

(B) Reaction of $[Re(CO)_2(NO)Cl_2]_2$ with β-Diketones.—Quite a few organometallic derivatives of β-diketones with transition metal carbonyl complexes have been described.[2] For group VII metals there have been reported some neutral complexes from the reaction of $Mn_2(CO)_{10}$ with hexafluoroacetylacetone[3] and their derivatives containing neutral monodentate ligands.[4] To the best of our knowledge, however, no such type of compound had been reported so far for carbonyl-nitrosyl complexes of rhenium or of other transition metals.

The reaction of $[Re(CO)_2(NO)Cl_2]_2$ with β-diketones of the type $RCOCH_2COR$ ($R = CH_3, CF_3, C_6H_5$) affords complexes of the formula $Re(CO)_2(NO)ACl$ (AH = β-diketone) (IV)

$$[Re(CO)_2(NO)Cl_2]_2 + 2AH \longrightarrow \underset{IV}{2Re(CO)_2(NO)ACl} + 2HCl \quad (3)$$

These products are crystalline solids, easily sublimable under vacuum, nonconducting in solution, diamagnetic, and soluble in most common organic solvents. Analytical data and selected infrared bands for these complexes are reported in Tables III and IV, respectively. The infrared spectra of IV and the proton nmr spectrum of the acetylacetone derivative support the structure



for these complexes. The infrared spectra, in fact, display two bands in the 1520–1630-cm^{-1} range which

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(2) For a comprehensive survey on organometallic derivatives of β-diketones with transition metal carbonyl complexes see F. Bonati, *Organometal. Chem. Rev.*, **1**, 379 (1966).

(3) M. Kilner and A. Wojcicki, *Inorg. Chem.*, **4**, 591 (1965).

(4) F. A. Hartmann, M. Kilner, and A. Wojcicki, *ibid.*, **6**, 34 (1967).

can be attributed to the C⩦O stretching vibrations in the acetylacetonato anion, besides the absorptions due to the terminal CO and NO stretching vibrations, indicating an oxygen-bridged chelate structure. Consistently, the ^{1}H nmr spectrum of the complex with acetylacetone displays two signals at τ 4.7 (weak) and 7.9 (strong), which can be assigned to the 3-C proton and to the methyl protons, respectively. The appearance of one single resonance for the methyl protons is probably due to the fact that the difference in chemical environment of the two methyl groups is not sufficient for two signals to be observed with the resolution afforded by our instrument.

Complexes IV with acetylacetone and dibenzoylmethane display a remarkable stability. No reaction was observed upon prolonged heating in the presence of nucleophilic agents. Such inertness is reminiscent of the behavior of disubstituted derivatives of rhenium pentacarbonyl chloride, $Re(CO)_3L_2Cl$,[5] which can be related to β-diketonato complexes IV by the presence of one CO ligand in the place of nitrosyl. In both cases it appears that coordination of two "hard"[6] groups (the two oxygen teeth of the chelating β-diketonate moiety in IV) highly stabilizes the "soft" terminal carbonyl ligands. By way of contrast, the hexafluoroacetylacetonato complex is highly reactive toward nucleophilic attack, probably owing to the deeply modified electron density distribution in the molecule. This in turn is reflected by the marked shifts of both terminal and ketonic carbonyl stretching bands caused by the strongly electronegative fluorine (Table IV). Reactivity studies are now under way and will be reported in a later publication.

Experimental Section

Materials.—Acetylacetone (C. Erba RP) and hexafluoroacetone (K & K) were distilled prior to use. Cyclooctene (Schuchardt), pyridine, 2-chloropyridine, triphenylarsine, triphenyl phosphite, and dibenzoylmethane (Fluka A.G.) were used without further purification. All other materials were reagent grade chemicals. Proton nmr spectra were recorded with a Perkin-Elmer A-60 spectrometer. $[Re(CO)_2(NO)Cl_2]_2$ was prepared as described previously.[1] All operations were carried out in a nitrogen atmosphere.

$[Re(CO)(NO)(C_8H_{14})Cl_2]_2$ (II).—A mixture of 0.34 g (0.5 mmol) of $[Re(CO_2)(NO)Cl_2]_2$ and 1 ml (8 mmol) of cyclooctene in 200 ml of carbon tetrachloride was refluxed for *ca.* 8 hr. The solution was then filtered and concentrated to a small volume under reduced pressure. Addition of *n*-hexane and standing in a refrigerator resulted in precipitation of the product II which was filtered off, air-dried, and recrystallized from carbon tetrachloride–hexane. A 0.28-g amount of II was obtained as a cream yellow crystalline powder (yield 65%).

$Re(CO)(NO)(py)_2Cl_2$.—A solution of II (0.15 g, 0.17 mmol) and excess anhydrous pyridine (0.14 g, 1.7 mmol) in 100 ml of 1,2-dichloroethane was refluxed for *ca.* 4 hr. After removal of dark residues by filtration, the solution was concentrated to a small volume under reduced pressure and the product was precipitated by addition of *n*-hexane. Recrystallization from dichloromethane–hexane gave 0.135 g of pure $Re(CO)(NO)(py)_2Cl_2$ as an orange-yellow solid (yield 81%).

$Re(CO)(NO)(2\text{-}Cl(py))_2Cl_2$.—A solution of 0.15 g of II and a tenfold molar excess of 2-chloropyridine (0.194 g) in 150 ml of 1,2-dichloroethane was refluxed for *ca.* 18 hr. After filtration and concentration of the deep green solution, the green crystalline product was obtained by precipitation with *n*-hexane and recrystallization from *n*-hexane–dichloromethane (10:1 v/v) (0.15 g, yield 94%).

$Re(CO)(NO)((C_6H_5)_3As)_2Cl_2$.—A solution of 0.15 g of II and a tenfold molar excess of triphenylarsine (0.52 g) in 150 ml of carbon tetrachloride was refluxed for *ca.* 12 hr. The sparingly soluble product slowly precipitated. This was filtered off and washed repeatedly with carbon tetrachloride and *n*-hexane (orange-yellow crystals, 0.25 g, yield 78%).

$Re(CO)(NO)((C_6H_5O)_3P)_2Cl_2$.—The preparation was carried out as above in 1,2-dichloroethane. After refluxing and concentrating, the white crystalline product was separated by addition of *n*-hexane, filtration, and recrystallization from *n*-hexane–dichloromethane (10:1 v/v) (yield 88%).

$Re(CO)_2(NO)(C_5H_7O_2)Cl$.—A solution of $[Re(CO)_2(NO)Cl_2]_2$ (0.3 g, 0.44 mmol) and of acetylacetone (0.2 g, 2 mmol) in 100 ml of carbon tetrachloride was refluxed for 2 days. After filtration and evaporation to a small volume, 100 ml of *n*-pentane was added and the unreacted starting complex which precipitated was removed by filtration. The filtrate was taken to dryness and the residue was sublimed at 60° (10^{-3} mm). A 0.22-g amount of fine lemon yellow crystals was obtained (yield 62%).

$Re(CO)_2(NO)(C_{15}H_{11}O_2)Cl$.—A solution of $[Re(CO)_2(NO)Cl_2]_2$ (0.5 g, 0.7 mmol) and of a stoichiometric deficiency of dibenzoylmethane (0.22 g, 1 mmol) in 200 ml of carbon tetrachloride was refluxed until its red color turned to yellow. This required *ca.* 8 days. After filtration and evaporation to a small volume under reduced pressure, 100 ml of *n*-hexane was added and the resulting suspension was set aside for 1 hr. After removal of the unreacted starting complex by filtration, the hexane solution was taken to dryness and the residue was redissolved in hot *n*-hexane. The filtered solution was taken to dryness and the process was repeated until a yellow solid resulted. The product does not sublime (0.32 g, yield 59% based on dibenzoylmethane).

$Re(CO_2)(NO)(C_5HF_6O_2)Cl$.—A solution of $[Re(CO)_2(NO)Cl_2]_2$ (0.15 g) containing an excess of freshly distilled hexafluoroacetylacetone (3 ml) in 100 ml of carbon tetrachloride was refluxed for 7 days, whereupon its yellow color turned to green. The solution was taken to dryness after filtration. From the residue, which also contained some unreacted starting complex, the bright green product was separated by sublimation at 40° (10^{-3} mm) (0.22 g, yield 10%).

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[5] F. Zingales, U. Sartorelli, and A. Trovati, *Inorg. Chem.*, **6**, 1246 (1967).

[6] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).