the radius of the metal ion decreases. Also the polar groups in the interior of the molecule should become better shielded as the molecule becomes more compact.

The difference between the half-temperaures ($T_{1/2}$) of the lighter and heavier members of a series of rare earth chelates is usually smaller for the tetrakis salts and solvated tris chelates than for anhydrous, unsolvated tris chelates. For example, $\Delta T_{1/2}$ is ~60° for Sm(pta)$_3$–Lu(pta)$_3$,[21] ~35° for Pr(thd)$_3$–Lu(thd$_3$,[1] and ~70° for Pr(fod)$_3$–Lu(fod)$_3$,[6] but for the solvated and tetrakis chelates listed in Table VI, $\Delta T_{1/2}$ for the Pr (or Nd or Sm) and Lu (or Yb) members of each series ranges from a maximum of ~40° to a minimum of ~10°, *i.e.*, to very little change in half-temperature as a function of ionic radius. One possible explanation of this behavior is that the adducts and tetrakis chelates are not as volatile as the unsolvated tris chelates and that dissociation must take place before vaporization occurs. However, the adducts and tetrakis chelates should become progressively more stable as the ionic radius decreases, due to a more favorable charge:radius ratio. There would thus be two opposing trends: the increasing volatility of LnL$_3$ with decreasing ionic radius would be countered by increasing stability of the less volatile salts and adducts. We emphasize that more experimental evidence is needed to confirm this explanation (gas-phase molecular weights would be particularly valuable). Mass spectra have shown that MLnL$_4$ (M is an alkali metal) chelates can sublime as ion pairs,[17,18] but to our knowledge little work has been done on the mechanism of volatilization of ammonium tetrakis chelates and solvated tris chelates.

Finally, it should be pointed out that water of hydration does not of necessity have a deleterious effect on the thermal stability of chelates. When the water is not coordinated to the metal or is coordinated but the metal–water bond is much more easily broken than the metal–diketonate bonds (*e.g.*, Ln(dfhd)$_3\cdot$2H$_2$O and Ln(fod)$_3\cdot$H$_2$O), the decomposition due to hydrolysis will be negligible.[23a]

[23a] NOTE ADDED IN PROOF.—Because these and other related compounds are highly soluble and are better Lewis acids (due to the electron. withdrawing fluorines) than any of the other nmr paramagnetic shift reagents yet reported, we have been examining them for use in nmr spectra clarification.

CONTRIBUTION NO. 1714 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Anomalous Reactions of Sterically Hindered Molybdenum Carbonyl Anions

BY S. TROFIMENKO*

Received July 6, 1970

The sterically hindered carbonyl anion HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3^-$ reacts with either ArSO$_2$Cl or ArSCl to yield the stable, monomeric red derivatives HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_2$SAr. A tungsten analog was prepared similarly as was the selenium analog HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_2$SeAr. The reaction of HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3^-$ with aryldiazonium salts leads to blue products assigned the structure HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3$Ar. Thionyl chloride reacts with (C$_2$H$_5$)$_4$NHB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3$ yielding a red precursor which, on contact with alumina, is converted to the green HB(3,5-(CH$_3$)$_2$pz)$_3$-MoCl$_2$O. Nitrosation of HB(3,5-(C$_2$H$_5$)$_2$pz)$_3$Mo(CO)$_3^-$ gave HB(3,5-(C$_2$H$_5$)$_2$pz)$_3$Mo(CO)$_2$NO.

One of the several advantages of the tris(1-pyrazolyl)borate ion, HB(pz)$_3^-$, over the cyclopentadienide ion as a ligand is that by appropriate substitution on the pyrazole rings one can alter the steric and/or electronic environment of the metal ion without destruction of the original symmetry of the parent ligand. It had been found before that presence of alkyl substituents in the 3 positions as in HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3^-$ increases the electron density on Mo, at the same time restricting the access to the metal by prospective reactants. The result is increased stability of derivatives, coupled with greater difficulty in effecting reactions that proceed through a sterically hindered transition state. For example, while nitrosation proceeds equally well [1] for the parent HB(pz)$_3$Mo(CO)$_3^-$, for the methylated system HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3^-$, and even for the still more hindered HB(3,5-(C$_2$H$_5$)$_2$pz)$_3$Mo(CO)$_3^-$, in the reaction with allyl bromide the 3,5-methylated species is inert under conditions[2] where the parent reacts rapidly. On the other hand, HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_2$-π-C$_3$H$_5$ has been prepared indirectly[3] and is quite stable. The present paper examines some other reactions of the HB(3,5-(CH$_3$)$_2$pz)$_3$-Mo(CO)$_3^-$ species, where unusual results were obtained.

HB(3,5-(CH$_3$)$_2$pz)$_3$Mo(CO)$_3^-$ reacted readily with *p*-toluenesulfonyl chloride at room temperature yielding as the main product an air-stable red solid which was assigned structure II (Ar = *p*-tolyl) on

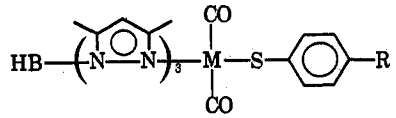
---

* Address correspondence to the Plastics Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Del. 19898.

(1) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).
(2) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 588 (1969).
(3) S. Trofimenko, *ibid.*, **91**, 3183 (1969).

TABLE I

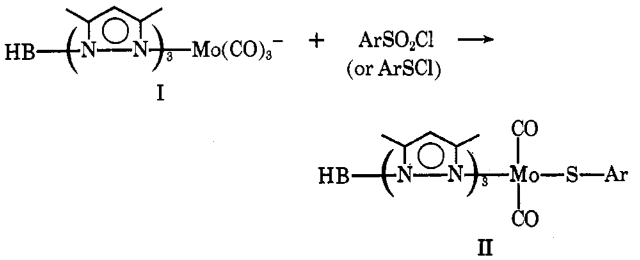
DATA FOR THE COMPOUNDS



Yield, % (method)	Mp, °C	M	R	% C		% H		% N		% X		Ir, cm^{-1}	Nmr[a]
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
26 (A)	~255 dec	Mo	CH_3	50.5	50.7	5.07	5.14	14.7	14.5	O, 5.60 S, 5.60 Mo, 16.8 (Mol wt 572)	O, 5.51 S, 5.52 Mo, 16.8 (Mol wt 558[b])	1961 1862	m 3.1, s 3.95, s 4:40, s 7.42, s 7.52, s 5.57, s 7.95, s 8.87 [4:1:2:6:3:3:3:6]
33 (A)	~250 dec	Mo	Br	43.4	43.2	4.08	4.01	13.2	13.1	Br, 12.6	Br, 12.0	1963 1867	m 2.9, s 3.90, s 4.37, s 7.37, s 7.52, s 8.85 [4:1:2:6:6:6]
29 (A) 33 (B)	235–238 dec	Mo	Cl	46.6	46.4	4.39	4.20	14.2	13.9			1959 1862	s 2.97, s 3.88, s 4.36, s 7.38, s 7.51, s 8.86 [4:1:2:6:6:6]
23 (A) 13 (B)	~230 dec	Mo	H	49.4	49.4	4.84	4.81	15.0	14.8			1959 1860	s 2.88, s 3.90, s 4.38, s 7.39, s 7.50, s 7.52, s 8.84 [5:1:2:6:3:3:6]
38 (B)	255–258 dec	W	Cl	40.5	40.2	3.82	3.69	12.3	12.1	Cl, 5.21 S, 4.70	Cl, 5.27 S, 5.00	1944 1841	m 3.12, s 3.93, s 4.27, s 7.33, s 7.58, s 8.48 [4:1:2:6:6:6]

[a] Listed are multiplicity and chemical shift in τ [area ratio]. [b] By vapor pressure osmometry in chloroform.

the basis of (1) elemental analysis and molecular weight determination which indicated an empirical formula $C_{24}H_{29}BMoN_6O_2S$, (2) the infrared spectrum which indicated the presence of two carbonyl groups (ν_{CO} 1961, 1862 cm^{-1}), and (3) the nmr spectrum which established the presence of one intact $HB(3,5\text{-}(CH_3)_2pz)_3^-$ ligand and of one *p*-tolyl group. The nmr spectrum also indicated C_2 rather than dynamic C_{3v} symmetry for this molecule, a finding not surprising in view of the known high rotational energy barrier of the $HB(3,5\text{-}(CH_3)_2pz)_3$ ligand. The arylmercapto structure was unexpected, since a sulfinate or sulfone product would be anticipated[4] or, perhaps, an M–Ar species resulting *via* extrusion of SO_2 from either of the first two structures. To test the generality of this reaction course, other arylsulfonyl chlorides were substituted for *p*-toluenesulfonyl chloride with identical results; *i.e.*, the reaction proceeded as follows (see Table I)



I

II

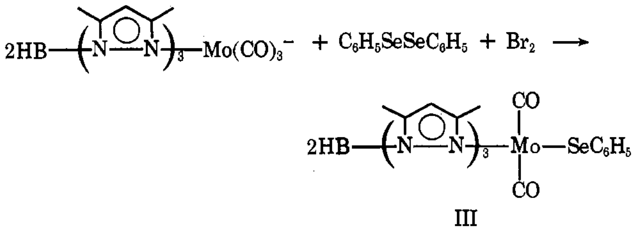
Yields were only moderate (20–30%), compatible with part of the molybdenum being oxidized to unidentified, water-soluble products at the same time deoxygenating $ArSO_2Cl$. Of pertinence here is the report[5] that $Mo(CO)_6$ reduces $ArSO_2Cl$ to ArSSAr. Whether some partially reduced species derived from $ArSO_2Cl$ reacts with I or whether an intermediate $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3SO_2Ar$ is produced first and then reduced by excess I is unknown.

As additional confirmation of structure II, the anion I was treated with ArSCl (Ar = phenyl, *p*-chlorophenyl), and in each case the products were identical in all respects with those obtained from the arysulfonyl chlorides.

No reaction of $C_5H_5Mo(CO)_3^-$ with arylsulfonyl chlorides has been reported, while the reaction with CH_3SO_2Cl yields[4] $C_5H_5Mo(CO)_3Cl$ and $[C_5H_5Mo(CO)_3]_2$. Of course, steric considerations prevent the existence of a dimer $[RB(pz)_3Mo(CO)_3]_2$. Steric reasons must also be responsible for the monomeric nature of compounds II, since the analogous $C_5H_5Mo(CO)_2SR$ compounds are always dimeric, regardless of whether R is an alkyl,[6] cycloalkyl,[7] or aryl[8] group.

In a single reaction, the tungsten analog of II, $HB(3,5\text{-}(CH_3)_2pz)_3W(CO)_2S\text{-}p\text{-}ClC_6H_4$, has been prepared. Its infrared and nmr spectra resembled those of the molybdenum compound, except that ν_{CO} was lowered by 15 and 21 cm^{-1}, as is generally the case in a pair of corresponding Mo and W compounds.

The selenium analog of II, $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_2SeC_6H_5$, was synthesized in good yields by the addition of bromine to a mixture of I and $C_6H_5SeSeC_6H_5$



III

This reaction might proceed *via* formation of C_6H_5SeBr which reacts with I; conversely, a species such as $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3Br$ might be formed first and then react with phenyl diselenide. Compound III was darker red and less soluble than II. Again, it was monomeric in contrast to its dimeric $[C_5H_5Mo(CO)_2SeC_6H_5]_2$ analog.[9]

Compound I also reacted anomalously with aryldi-

---

(4) M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).

(5) H. Alper, *Angew. Chem.*, **81**, 706 (1969).

(6) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(7) P. M. Treichel and G. R. Wilkes, *Inorg. Chem.*, **5**, 1182 (1966).

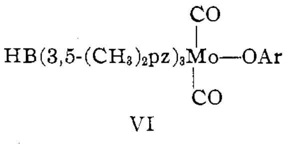
(8) R. Havlin and G. R. Knox, *Z. Naturforsch. B*, **21**, 1108 (1966).

(9) E. W. Tillay, E. D. Schermer, and W. H. Baddley, *Inorg. Chem.*, **7**, 1925 (1968).

azonium ions, ArN_2^+ (Ar = phenyl or *p*-nitrophenyl). In contrast to the $C_5H_5Mo(CO)_3^-$ system[10] or the parent ligand[11] $HB(pz)_3Mo(CO)_3^-$, both of which react with extrusion of CO to yield the red arylazo derivatives, blue compounds were obtained accompanied by evolution of 1 equiv of gas. Nmr spectra established the presence of one intact HB(3,5-$(CH_3)_2$-pz)$_3$ ligand and of the appropriate aryl group, and indicated overall C_2 symmetry for the molecule. The compounds were monomeric, contained three oxygens per molecule (apart from the nitro group in one of them), and contained no azo group nitrogen. Unfortunately, analytical results did not distinguish among possibilities V, VI, and VII.

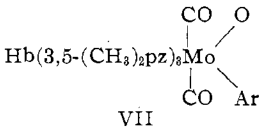
HB(3,5-$(CH_3)_2$pz)$_3$Mo(CO)$_3$Ar

V



$$\mathrm{HB(3,5\text{-}(CH_3)_2pz)_3\overset{CO}{\underset{CO}{Mo}}{-}OAr}$$

VI



$$\mathrm{Hb(3,5\text{-}(CH_3)_2pz)_3\overset{CO}{\underset{CO}{Mo}}\begin{smallmatrix}O\\ \\ Ar\end{smallmatrix}}$$

VII

The infrared spectra were drastically different from those of, *e.g.*, II, III, or $HB(pz)_3M(CO)_2N{=}NAr$, all of which have two strong bands of about equal intensity. The blue compound derived from $C_6H_5N_2^+$ had three bands: 1956 (w), 1865 (vs), and 1840 cm^{-1} (w). That from *p*-nitrodiazonium salt had two: 1966 (w) and 1877 cm^{-1} (vs). These data would point to structure V, which is also consistent with the loss of 1 equiv of N_2 as the only gas evolved, and hence retention of all three carbonyl groups. The color of compound V is, nevertheless, baffling. The most closely related known compound is $C_5H_5W(CO)_3C_6H_5$ which was prepared in poor yield from $C_5H_5W(CO)_3^-$ and phenyldiazonium ion[12] and in better yield from phenyliodonium ion[13] and the structure of which has been established by X-ray study.[14] The molybdenum analog could not be prepared by the above methods. That compound is yellow, is unstable in solution, and on heating to about 150° rearranges to the dimer $[C_6H_5C_5H_4W(CO)_3]_2$. It is noteworthy that $C_5H_5W(CO)_3C_6H_5$ has only two ν_{CO} although their relative intensities are not given.

It appears thus that structure V agrees best with the evidence on hand. Why the course of the reaction changes so drastically on going from the parent HB-(pz)$_3$MoCO$_3$)$^-$ to the methylated derivative I is uncertain. The first step in both instances is probably the formation of an $-Mo(CO)_3N{=}NAr$ species which in one case proceeds to lose CO and in the present case proceeds to lose N_2. No persuasive rationale can be advanced for this behavior. Molecular models indicate that the phenyl group can be accommodated without undue strain by fitting flatly between two pyrazolyl bridges. Still, the last word on the structure of V will have to be said by an X-ray structure determination.

The reaction of $(C_2H_5)_4$NHB(3,5-$(CH_3)_2$pz)$_3$Mo-(CO)$_3$ with thionyl chloride in dichloromethane produced in fair yield an unidentified red solid which on contact with acid-washed alumina changed to a green material identified as the oxydichloride species HB-(3,5-$(CH_3)_2$pz)$_3$MoCl$_2$O. The same compound was also obtained by the reaction of KHB(3,5-$(CH_3)_2$pz)$_3$ with $MoOCl_3$. This underscores again the ability of I to act as a reducing agent.

Experimental Section

The arylsulfur monochlorides were prepared from the corresponding mercaptans by the method of Lecher and Holschneider.[15] The arylmercapto compounds were prepared by the two general methods exemplified below (see Table I).

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum *p*-Chlorophenylmercaptide. (A) **Arylsulfonyl Chloride Method.**—To 0.1 mol of KHB(3,5-$(CH_3)_2$pz)$_3$Mo(CO)$_3$, prepared *in situ* in 250 ml of DMF, was added a freshly made solution of 21.1 g (0.1 mol) of *p*-chlorobenzenesulfonyl chloride. Gas evolution proceeded at room temperature and stopped after ~4 l. was evolved. The reaction mixture was poured into 2 l. of water and the red precipitate was extracted with methylene chloride. The extracts were chromatographed on alumina eluting with a 1:1 hexane–ether mixture. The red product was obtained in 17 g (29%) yield. It was purified by recrystallization from chlorobenzene. Its properties are listed in Table I.

(B) **Arylsulfur Chloride Method.**—To 0.1 mol of KHB(3,5-$(CH_3)_2$pz)$_3$Mo(CO)$_3$, prepared *in situ* in 250 ml of DMF, was added 17.9 g (0.1 mol) of *p*-chlorophenylsulfur chloride. A blood red solution was obtained as 2.4 l. of gas was evolved. The solution was poured into 2 l. of water and the precipitated product was extracted with methylene chloride. The extracts were chromatographed on alumina, as above, and the product, identical in all respects with that from procedure A, was obtained in 19.6 g (33.3%) yield.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratotricarbonyl-*p*-nitrophenylmolybdenum.—To a suspension of 60.7 g of $(C_2H_5)_4$N-HB(3,5-$(CH_3)_2$pz)$_3$Mo(CO)$_3$ (0.1 mol) in 600 ml of methylene chloride was added in portions 25.6 g (0.1 mol) of *p*-nitrobenzenediazonium fluoroborate. The system was closed and gas evolution was measured with a wet-test meter. Aboug 2.4 l. of gas was evolved (0.1 mol) and the reaction mixture turned blue. It was stirred with 1 l. of water and the organic layer was chromatographed on alumina collecting the blue band. Stripping, trituration with methanol, and washing the residue with ether gave 20.3 g (34.0%) of blue-black crystals. The material was recrystallized twice from toluene; mp 229–231° dec.

In addition, a slower moving red band was obtained in 4.8 g yield. Spectral data supported the presence of an NH_2 group in place of NO_2. It was not investigated further.

Anal. Calcd for $C_{24}H_{26}BMoN_7O$ (main product): C, 48.1; H, 4.34; N, 16.3; O, 13.3; mol wt 599. Found: C, 48.3; H, 4.33; N, 16.3; O, 13.3; mol wt 588 (by vapor pressure osmometry in chloroform). Ir (cyclohexene): 1966 (w), 1877 cm^{-1} (vs). Nmr: q 1.55, singlets at 4.04, 4.16, 7.52, 7.57, 7.62, and 7.97 in 4:1:2:3:6:3:6 ratio. Uv: broad peak ~656 (ϵ 2720) 365 (sh) (ϵ 2490), 270 mμ (ϵ 27,900).

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratotricarbonylphenylmolybdenum.—To 0.1 mol of KHB(3,5-$(CH_3)_2$pz)$_3$Mo(CO)$_3$, prepared *in situ* in 250 ml of DMF, was added a DMF solution of freshly prepared phenyldiazonium fluoroborate. There was

---

[10] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

[11] S. Trofimenko, *ibid.*, **8**, 2675 (1969).

[12] A. N. Nesmeyanov, Yu. A. Chapovskii, B. V. Lokshin, A. V. Kisin, and L. G. Makarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 449 (1968).

[13] A. N. Nesmeyanov, Yu. A. Chapovskii, B. V. Lokshin, A. V. Kisin, and L. G. Makarova, *Dokl. Akad. Nauk SSSR*, **171**, 637 (1966).

[14] V. A. Semion, Yu. A. Chapovskii, Yu. T. Struchkov, and A. N. Nesmeyanov, *Chem. Commun.*, 666 (1968).

[15] H. Lecher and F. Holschneider, *Ber.*, **57**, 755 (1924).

2.5 l. of gas evolved at room temperature. The reaction mixture was poured into 1 l. of water, and the product was extracted with methylene chloride and chromatographed as in the preceding experiment. There was obtained 20.4 g (36.8%) of bluish solid which was recrystallized from methylene chloride–ethanol; mp 226–230°.

Anal. Calcd for $C_{24}H_{27}BMoN_6O_3$: C, 52.0; H, 4.87; Mo, 17.3; N, 15.1; O, 8.67; mol wt 554. Calcd for $C_{23}H_{27}BMoN_6O_3$: C, 51.0; H, 4.99; Mo, 17.7; N, 15.5; O, 8.87; mol wt 542. Found: C, 51.0; H, 4.97; Mo, 17.7; N, 14.8; O, 8.75; mol wt 539 (osmometry in chloroform). Ir (cyclohexane): 1956 (w), 1865 (vs), 1840 cm^{-1} (w). Nmr: m ~2.8; m ~3.4; singlets at 5.16, 5.25, 8.60, 8.66, 8.67, and 9.02 in 2:3:1:2:3:6:3:6 ratio.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratooxomolybdenum Dichloride.—Into a stirred slurry of 31 g (0.05 mol) of $(C_2H_5)_4N$-$HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3$ in 300 ml of methylene chloride was added dropwise thionyl chloride until all gas evolution ceased. The slurry was stirred with 500 ml of water and the red organic layer was separated. It was diluted to 500 ml with methylene chloride and slurried with about 250 ml of Merck acid-washed alumina. When the color changed to green, the mixture was filtered, and the filtrate was stripped yielding a green solid which was stirred with CH_3OH and filtered. There was obtained 14.0 g (58.4%) of green crystals. After recrystallization from chlorobenzene, the product decomposes gradually from 350°.

Anal. Calcd for $C_{15}H_{22}BCl_2MoN_6O$: C, 37.5; H, 4.58; Cl, 14.8; Mo, 20.0; N, 17.5; O, 3.33; mol wt 480. Found: C, 37.4; H, 4.51; Cl, 15.4; Mo, 20.0; N, 17.3; O, 3.29; S absent; mol wt 482 (by osmometry in chloroform). The infrared spectrum is devoid of carbonyl bands but has a strong BH spike at ~2580 cm^{-1}.

Hydrotris(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum Phenylselenide.—To a solution of 0.02 mol of $KHB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3$ prepared *in situ* was added 0.01 mol of phenyl diselenide, followed by 0.01 mol of bromine dissolved in 20 ml of carbon tetrachloride. The mixture was heated whereupon it started turning red and the solids dissolved. When a total of 0.6 l. of gas was evolved, the solution was poured into water. The product was extracted with methylene chloride and the extracts were chromatographed on alumina yielding 3.6 g (61%) of a dark red solid. It was recrystallized from dimethylformamide; mp 258–260° dec.

Anal. Calcd for $C_{22}H_{27}BMoN_6O_2Se$: C, 44.5; H, 4.56; N, 14.1. Found: C, 44.3; H, 4.67; N, 13.8. Ir (cyclohexane): 1957, 1859 cm^{-1}. Nmr: m 2.80; singlets at 3.88, 4.33, 7.34, 7.54, and 8.82 in 5:1:2:6:6:6 ratio.

Hydrotris(3,5-diethyl-1-pyrazolyl)boratodicarbonylnitrosylmolybdenum.—This compound was prepared in 28% overall yield by a method analogous to that employed for the 3,5-dimethyl analog,[1] but employing 3,5-diethylpyrazole[16] as the starting material. The product was recrystallized from toluene; it crystallizes as an orange solvate. Drying gives yellow crystals, mp 238–240°.

Anal. Calcd for $C_{23}H_{24}BMoN_7O_3$: C, 49.0; H, 6.04; N, 17.4. Found: C, 48.7; H, 6.18; N, 17.4. Ir (cyclohexane): 2014 (CO), 1924 (CO), and 1670 cm^{-1} (NO).

---

(16) D. S. Noyce, E. Ryder, Jr., and B. H. Walker, *J. Org. Chem.*, **20**, 1684 (1955).

CONTRIBUTION FROM THE CATTEDRA DI CHIMICA,
FACOLTÁ DI INGEGNERIA, UNIVERSITÁ DI PADOVA, PADUA, ITALY

Halogen-Bridged Rhenium Carbonyl Nitrosyl Complexes and Derivatives

BY FRANCO ZINGALES, ALDO TROVATI, FRANCO CARIATI, AND PAOLO UGUAGLIATI*

Received February 27, 1970

The new carbonyl nitrosyl complex of rhenium $[Re(CO)_2(NO)Cl_2]_2$ is obtained by the reaction of $[Re(CO)_4Cl]_2$ with nitric oxide in the presence of hydrogen chloride. The analogous bromo and iodo derivatives are produced by metathesis of the chloro complex with potassium bromide or iodide. These halide-bridged dimeric compounds undergo facile bridge-splitting reactions by neutral ligands (L) to give monomeric complexes of type $Re(CO)_2(NO)X_2L$ (L = pyridine, 4-picoline, 3,4-lutidine, tributylphosphine, pyridine oxide, triphenylphosphine oxide, tetrahydrothiophene and X = Cl; L = pyridine and X = Br, I). The chloride derivatives can also be obtained by the reaction of $Re(CO)_4ClL$ or $Re(CO)_3ClL_2$ with nitric oxide in the presence of hydrogen chloride. All of these carbonyl nitrosyl complexes display remarkable stability. Infrared spectra are reported. Based on these data, probable structures for these complexes are proposed.

Introduction

Comparably few nitrosyl complexes of group VIIa elements have been reported so far.[1] Most of these are manganese compounds, which can be grouped into three main types: (i) carbonyl nitrosyl complexes such as $Mn(CO)_4(NO)$,[2,3] $Mn(CO)(NO)_3$,[4] $Mn(CO)_3(NO)L$,[5-7] $Mn(CO)_2(NO)L_2$[5-7] (where L is a monodentate ligand such as tertiary phosphine, phosphite, etc.), and $Mn_2(CO)_7(NO)_2$;[2] (ii) simple nitrosyl complexes such as $Mn(NO)_3L$[5,7] and $Mn(NO)_2L_2X$;[5,6] (iii) cyclopentadienyl nitrosyl complexes such as $(C_5H_5)Mn(CO)_2(NO)^+$,[8] $[(C_5H_5)Mn(CO)(NO)]_2$,[9] $(C_5H_5)Mn(OCOCH_3)(CO)(NO)$,[10] and $(C_5H_5)_3Mn_2(NO)_3$.[11]

---

* To whom correspondence should be addressed at the Centro Chimica Technologia Composti Metallorganici Elementi Transizione del CNR, Bologna, Italy.

(1) For a comprehensive survey on transition metal nitrosyl complexes, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(2) P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 2593 (1961).

(3) H. Wawersik and F. Basolo, *Inorg. Chem.*, **6**, 1066 (1967).

(4) C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960).

(5) W. Hieber and H. Tengler, *Z. Anorg. Allg. Chem.*, **318**, 136 (1962).

(6) W. Beck and K. Lottes, *Ber.*, **98**, 2657 (1965).

(7) H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, **89**, 4626 (1967).

(8) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(9) R. B. King and M. B. Bisnette, *J. Amer. Chem. Soc.*, **85**, 2527 (1963).

(10) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, **4**, 256 (1965).

(11) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).