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Complexes of *cis*-1,2-Bis(dimethylarsino)ethylene. II. Carbonyls and Nitrosyls

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The reactions of *cis*-1,2-bis(dimethylarsino)ethylene (*cis*-edas) and *o*-phenylenebis(dimethylarsine) (das) with the carbon monoxide derivatives of chromium, molybdenum, tungsten, and nickel and with $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ have been investigated. The new complexes prepared in this study include $Cr(CO)_4$(*cis*-edas), $Mo(CO)_4$(*cis*-edas), $W(CO)_4$(*cis*-edas), $Ni(CO)_2$(*cis*-edas), $Fe(NO_2$(das), and Co(CO)(NO)(das). The ligands and their complexes were characterized by means of infrared spectroscopy, mass spectroscopy, and nmr spectroscopy. Complexes of *cis*-1,2-bis(dimethylarsino)ethylene with iron and cobalt nitrosyls proved to be too unstable to isolate. An improved method for the preparation of $Cr(CO)_4$(das), $Mo(CO)_4$(das), and $W(CO)_4$(das) is also reported.

Introduction

Tertiary arsine ligands are known to stabilize metals in both high and low oxidation states. The preparation and properties of complexes of Fe(III), Fe(II), Co(III), Ti(IV), Pd(II), Pt(II), and Cu(I) with *cis*-1,2-bis(dimethylarsino)ethylene (*cis*-edas) have been reported previously.[2-4] The complexes of *cis*-1,2-bis(dimethylarsino)ethylene with these metals in higher oxidation states have chemical and physical properties which are closely similar to those of *o*-phenylenebis(dimethylarsine) (das). Nickel carbonyl and the group VI metal carbonyl complexes with *o*-phenylenebis(dimethylarsine) are well characterized.[5,6] However, the complexes of these metal carbonyls with *cis*-1,2-bis(dimethylarsino)ethylene have not as yet been investigated. The complexes of *o*-phenylenebis(dimethylarsine) and of *cis*-1,2-bis(dimethylarsino)ethylene with the mixed carbonyl–nitrosyl derivatives of iron and cobalt have not been previously reported. Accordingly, the *cis*-1,2-bis(dimethylarsino)ethylene derivatives of the group VI carbonyls, nickel carbonyl, and the iron and cobalt nitrosyls have now been prepared and characterized.

Experimental Section

Materials and Analyses.—Chromium, molybdenum, tungsten, and iron carbonyls were obtained from Alfa Inorganics, Inc., while nickel carbonyl was obtained from the Matheson Co., Inc. Tricarbonylnitrosylcobalt was prepared according to the method of Gilmont.[7] Dicarbonyldinitrosyliron was prepared using the method outlined by King.[8] Both the cobalt and iron nitrosyl complexes decompose slowly on standing and were therefore redistilled prior to their use. The preparation of the ligands *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsino)ethylene has been described previously.[2,9] The solvents used were reagent grade and deaerated using oxygen-free nitrogen. The nitrogen was purified by passing it over a bed of BTS catalyst obtained from BASF for oxygen removal and then over molecular sieve pellets to remove traces of water. The compounds were analyzed by Huffman Laboratories, Wheatridge, Colo.

The infrared spectra were obtained from KBr disks using a Perkin-Elmer 337 or Beckman IR 12 spectrometer. The nmr spectra were measured on a Varian A-60 or HA100, while the mass spectra were recorded on a Perkin-Elmer Hitachi RMU-6e double-focusing mass spectrometer.

Tetracarbonyl[*cis*-1,2-bis(dimethylarsino)ethylene]molybdenum(0).—A 250-ml Schlenk tube[8] was charged with 0.6 g of $Mo(CO)_6$ in 25 ml of tetrahydrofuran and 1.0 g of *cis*-1,2-bis(dimethylarsino)ethylene was added. The solution was heated to 64° and refluxed for 24 hr. After cooling, 200 ml of water was added to give an oily white precipitate. The precipitate was collected by filtration, sublimed at 90° (0.1 mm), and recrystallized from hexane. The white crystals were dried under vacuum to yield 1.1 g of the complex. The solid complex was air stable and soluble in most organic solvents. Solutions of the complex were easily oxidized in air and had to be handled under nitrogen. *Anal.* Calcd for $C_{10}H_{14}As_2O_4Mo$: C, 27.1; H, 3.2; mol wt 446 (calcd for ^{98}Mo). Found: C, 27.1; H, 3.3; mol wt 446; mp 117–118° (uncor).

Tetracarbonyl[*cis*-1,2-bis(dimethylarsino)ethylene]chromium(0).—A 250-ml Schlenk tube was charged with 0.7 g of $Cr(CO)_6$ in 25 ml of diglyme, 10 ml of tetrahydrofuran, and 1.2 g of *cis*-1,2-bis(dimethylarsino)ethylene. The solution was heated to 130° and refluxed for 24 hr. To the yellow solution, 200 ml of water was added and a pale yellow oily precipitate formed. This precipitate was collected by filtration, sublimed at 100° (0.1 mm), and recrystallized twice from hexane. The yellow crystals were dried under vacuum to yield 0.3 g of a yellow crystalline complex. This complex has properties similar to its molybdenum analog. *Anal.* Calcd for $C_{10}H_{14}As_2CrO_4$: C, 30.0; H, 3.5; mol wt 400. Found: C, 30.5; H, 3.8; mol wt 400; mp 119–121° (uncor).

Tetracarbonyl[*cis*-1,2-bis(dimethylarsino)ethylene]tungsten(0).—A 250-ml Schlenk tube was charged with 0.2 g of $W(CO)_6$ in 40 ml of diglyme, 10 ml of tetrahydrofuran, and 0.2 g of *cis*-1,2-bis(dimethylarsino)ethylene. The solution was refluxed at 150° for 48 hr using an oil bath. After cooling, 150 ml of water was added to precipitate a white solid. After collection by filtration, the solid was sublimed at 110° (0.1 mm), recrystallized from hexane, and resublimed yielding 0.075 g of the complex. *Anal.* Calcd for $C_{10}H_{14}As_2O_4W$: C, 22.6; H, 2.6; mol wt 532. Found: C, 22.8; H, 3.4; mol wt 532, mp 136–138° (uncor).

Dinitrosyl[*o*-phenylenebis(dimethylarsine)]iron.—A 250-ml Schlenk tube containing $Fe(CO)_2(NO)_2$ (0.2 g), *o*-phenylenebis(dimethylarsine) (0.3 g), and 50 ml of tetrahydrofuran was heated to 60° for 12 hr with magnetic stirring. After cooling, 150 ml of water was added and a dark precipitate formed. The precipitate was collected by filtration and sublimed at 160° (0.4 mm), to yield 0.035 g of black crystalline product. The complex was soluble in ethers and decomposed in hexane. The solid slowly oxidized in the air. *Anal.* Calcd for $C_{10}H_{16}As_2FeN_2O_2$: C, 29.9; H, 4.0; N, 7.0; mol wt 402 (calcd using ^{56}Fe). Found: C, 28.6; H, 4.6; N, 6.5; mol wt 402; mp 160–162° (uncor).

Carbonylnitrosyl[*o*-phenylenebis(dimethylarsine)]cobalt.—A 250-ml Schlenk tube containing $Co(CO)_3NO$ (0.35 g), *o*-phenyl-

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[9] R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal. Chem.*, **7**, 285 (1968).

enebis(dimethylarsine) (0.55 g), and 50 ml of tetrahydrofuran was stirred for 4 hr and then heated to 60° for 12 hr. After cooling 150 ml of water was added and a dark precipitate formed. This precipitate was removed by filtration and sublimed at 120° (0.4 mm) to yield 0.35 g of red crystals. After drying under vacuum, the red complex was found to be soluble in most organic solvents but decomposed in hexane. The solid is air sensitive. *Anal.* Calcd for $C_{11}H_{16}As_2CoNO_2$: C, 32.8; H, 4.0; N, 3.5; mol wt 403. Found: C, 32.9; H, 3.3; N, 3.3; mol wt 403; mp 140–142° (uncor).

Dicarbonyl[*cis*-1,2-bis(dimethylarsino)ethylene]nickel(0).—A 75-ml Schlenk tube was purged with nitrogen and charged with $Ni(CO)_4$ (0.2 g), *cis*-1,2-bis(dimethylarsino)ethylene (0.1 g), and 10 ml of pentane. The temperature was maintained at °0 by use of an ice–water bath and the solution was stirred for 8 hr. Then the solvent was removed by vacuum distillation while the temperature was maintained at 0°. A white oily solid formed which was very air sensitive and decomposed at room temperature even under a nitrogen atmosphere. All attempts at purification resulted in even more impure materials due to decomposition. The impure material from this reaction could be stored at −40° for appreciable periods of time. The infrared spectrum of this material showed only two carbonyl bands at 2000 and 1934 cm^{-1}. The mass spectrum gave a parent ion at *m/e* 350 (calcd 350).

Tetracarbonyl[*o*-phenylenebis(dimethylarsine)]molybdenum(0).—The tetracarbonyl complexes of chromium, molybdenum, and tungsten ($M(CO)_4$das), have all been reported previously.[5] The molybdenum compound was required for comparison with the complexes of *cis*-1,2-bis(dimethylarsino)ethylene. The method for preparing the molybdenum compound described below is a more convenient method and gives a product of higher initial purity than the method described in the literature and also can be used to prepare the chromium and tungsten complexes.

A 250-ml Schlenk tube mixture consisting of $Mo(CO)_6$ (1.0 g), *o*-phenylenebis(dimethylarsine) (2.4 g), 40 ml of diglyme, and 10 ml of tetrahydrofuran was refluxed at 125° for 24 hr using an oil bath. The large amount of diglyme allowed the reaction to be carried out at the higher temperatures required for this reaction, while the presence of tetrahydrofuran was necessary to prevent loss of the carbonyl by sublimation into the reflux condenser. After cooling the reaction mixture, 200 ml of water was added producing a white precipitate. After collecting the precipitate by filtration, it was sublimed at 130° (0.1 mm) and then recrystallized from hexane. The 1.3 g of complex obtained from this reaction was dried under vacuum. The nickel complex was prepared similarly. *Anal.* Calcd for $C_{14}H_{16}As_2MoO_4$: C, 34.0; H, 3.3; mol wt 496 (calcd using ^{98}Mo). Found: C, 34.4; H, 3.4; mol wt 496; mp 153–154° (lit.[5] mp 158°).

Results and Discussion

Nyholm[5] has prepared the compounds $M(CO)_4(das)$ and $M(CO)_2(das)_2$ where M is Cr, Mo, and W. The complexes of *o*-phenylenebis(dimethylarsine) were prepared by the reaction between the ligand and the metal carbonyl in sealed tubes at temperatures between 150 and 240°. The reactions were carried out in sealed tubes in order to prevent the loss of the metal carbonyl by sublimation. Since the carbon monoxide liberated in the sealed tubes requires higher temperatures for the displacement reactions, alternative methods for the preparation of the carbonyl complexes of *o*-phenylenebis(dimethylarsine) were investigated. It was found that the group VI carbonyls react readily with *o*-phenylenebis(dimethylarsine) in diglyme. Tetrahydrofuran was added to these solutions to prevent the loss of the hexacarbonyls from the reaction vessels. Using mixtures of diglyme and tetrahydrofuran, it was possible to carry out the displacement reactions at temperatures 50–75° lower than was necessary for the sealed-tube reactions. When the reactions between *cis*-1,2-bis(dimethylarsino)ethylene and the group VI carbonyls were carried out at high temperatures (150–200°) under conditions similar to those initially used for the preparation of the *o*-phenylenebis(dimethylarsine) complexes, it was found that no pure compounds could be isolated from the reactions. The method described above was therefore developed and utilized for the preparation of the complexes of *cis*-1,2-bis(dimethylarsino)ethylene. The ligand *cis*-1,2-bis(dimethylarsino)ethylene reacts with the group VI metal carbonyls at temperatures between 60 and 150° to form the compounds $M(CO)_4$(*cis*-edas) (M = Cr, Mo, W). The compounds obtained from these reactions were white or pale yellow solids melting between 117 and 138°. The complexes are insoluble in water and soluble in most organic solvents. As solids, the compounds are stable but are readily oxidized in solution. Several attempts were made to prepare the dicarbonyl compounds $M(CO)_2$(*cis*-edas)$_2$. Unfortunately, the higher temperatures required for these reactions produced only insoluble brown tars which were not further characterized.

The compounds were characterized by elemental analyses and by nmr, ir, and mass spectroscopy. The mass spectra of the complexes and the ligands *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsino)ethylene were particularly useful in characterizing the products. The carbonyl stretching frequencies (Table I) of the complexes of *cis*-1,2-bis(dimethylarsino)ethylene have somewhat lower frequencies than those of the *o*-phenylenebis(dimethylarsine) counterparts. This effect is probably due to the decreased back-π-bonding with the olefin ligand. This observation is also consistent with the decreased stability of the complexes of *cis*-1,2-bis(dimethylarsine). There should be greater π interaction between the $As(CH_3)_2$ groups and the olefinic carbons compared with those of the aromatic ring. This π interaction should increase the π-electron density on the arsenics of *cis*-1,2-bis(dimethylarsino)ethylene relative to *o*-phenylenebis(dimethylarsine) and consequently decrease the amount of π-electron donation from the metal to the arsenic ligand. In turn, this should lead to lower CO stretching frequencies because of the increased back-π-bonding between the metal and the CO group.

TABLE I
INFRARED SPECTRAL DATA FOR SUBSTITUTED GROUP VI CARBONYLS

Compd	CO str freq, cm^{-1}	Ref
$Cr(CO)_4$(*cis*-edas)	2010, 1935, 1900, 1880	*a*
$Cr(CO)_4$(das)	2012, 1922, 1898	*b*
$Cr(CO)_2(das)_2$	1845, 1771	*b*
$Mo(CO)_4$(*cis*-edas)	2020, 1905, 1890, 1870	*a*
$Mo(CO)_4$(das)	2026, 1938, 1923, 1914	*b*
$Mo(CO)_4$(ffars)	2025, 1937, 1896	*c*
$Mo(CO)_2(das)_2$	1859, 1786	*b*
$W(CO)_4$(*cis*-edas)	2009, 1903, 1873, 1852	*a*
$W(CO)_4$(das)	2066, 1923, 1905, 1885	*b*
$W(CO)_2(das)_2$	1850, 1774	*b*

[a] This work. [b] Reference 5. [c] W. R. Cullen, P. S. Dhaliwa, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).

The nmr spectra of the *cis*-1,2-bis(dimethylarsino)ethylene complexes of the group VI carbonyls in $CDCl_3$ with internal TMS as a reference are summarized in Table II. All of the protons were deshielded and shifted downfield 0.5 and 0.2 ppm relative to the free ligand. However, there was no obvious correlation between the nmr shifts and other physical parameters.

There have been relatively few studies of the mass

TABLE II
NMR CHEMICAL SHIFTS *cis*-1,2-BIS(DIMETHYLARSINO)ETHYLENE COMPLEXES (PPM FROM INTERNAL TMS)

Compd	Solvent	Methyl protons	Olefinic protons
$Cr(CO)_4$(*cis*-edas)	$CDCl_3$	1.5 (6H)	7.4 (1H)
$Mo(CO)_4$(*cis*-edas)	$CDCl_3$	1.5 (6H)	7.5 (1H)
$W(CO)_4$(*cis*-edas)	$CDCl_3$	1.6 (6H)	7.2 (1H)
trans-[$CoBr_2$(*cis*-edas)$_2$]Br	$(CD_3)_2SO$	1.6 (6H)	7.4 (1H)

spectra of the tertiary arsines and phosphines.[10,11] One feature of the mass spectra of those tertiary phosphines and arsines which have been examined is the ease of cleavage of the C–As and C–P bonds and the migration of hydrogen atoms. Both processes are important in the fragmentation of the tertiary arsines and their complexes. *cis*-1,2-Bis(dimethylarsino)ethylene has a mass spectrum which consists of the parent molecular ion at *m/e* 236 and the most intense ion in the spectrum at *m/e* 221 corresponding to the loss of one methyl group. The mass spectra are summarized in Table III.

The mass spectra of the group VI carbonyl complexes of *cis*-1,2-bis(dimethylarsino)ethylene have many features in common with those of the parent ligand. The mass spectra of the chromium, molybdenum, and tungsten complexes $M(CO)_4$(*cis*-edas) are very similar. All have an abundant parent ion and abundant ions corresponding to the loss of one, two, three, and four carbonyl groups. Ion fragments corresponding to $(P - CH_3)^+$ ions are also observed as were species containing two arsenic atoms and no transition metal.

The derivatives of the isoelectronic series of carbonyl–nitrosyl complexes $Ni(CO)_4$, $CoNO(CO)_3$, and $Fe(NO)_2(CO)_2$ were more difficult to characterize. The only complex of *cis*-1,2-bis(dimethylarsino)ethylene which could be isolated for even short periods of time was $Ni(CO)_2$(*cis*-edas). While the *o*-phenylenebis(dimethylarsine) complexes of this series of carbonyls and nitrosyls were readily isolated, the nitrosyls Co(CO)(NO)(das) and $Fe(NO)_2$(das) were much less stable than any of the other complexes prepared in this research. In order to develop a suitable method for isolating the complex $Ni(CO)_2$(*cis*-edas) the synthesis of the complex $Ni(CO)_2$(das), previously reported by Nyholm,[6] was reinvestigated to find the mildest conditions possible for the preparation of this complex. It was found that nickel carbonyl reacts essentially quantitatively with *o*-phenylenebis(dimethylarsine) at 0°. This method was used to prepare the complex $Ni(CO)_2$(*cis*-edas). The reaction between nickel carbonyl and *cis*-1,2-bis(dimethylarsino)ethylene takes place slowly in pentane at 0° with the evolution of 2 equiv of carbon monoxide per mole of arsine ligand followed by decomposition. The kinetics of this reaction and the reaction between nickel carbonyl and *o*-phenylenebis(dimethylarsine) have been studied by Plankey.[12] Both reactions proceed at the same initial rate under similar conditions. The reaction between nickel carbonyl and *o*-phenylenebis(dimethylarsine) terminated when the solution was depleted of either reagent. However, the reaction between nickel carbonyl and *cis*-1,2-bis(dimethylarsino)ethylene released additional carbon monoxide even in the presence of excess nickel carbonyl. The release of additional carbon monoxide (>2:1) was slow in comparison to the initial reaction. However, no conditions were found which would completely suppress this slow reaction, so that an analytically pure compound could not be isolated. However, if the pentane is removed from the reaction product at 0°, the white solid obtained is reasonably pure. A mass spectrum of this solid shows a peak in the mass spectrum at *m/e* 350, which is the expected value for the parent ion $Ni(CO)_2$(*cis*-edas)$^+$. There were also ions at *m/e* 322 and 294 corresponding to the loss of one and two carbonyl groups from the parent ion. An infrared spectrum of the white solid initially had only two carbonyl stretching frequencies at 2000 and 1935 cm^{-1} compared with those observed for $Ni(CO)_2$(das) at 1996 and 1931 cm^{-1} (Table I). On standing, the white solid converted to a brown material with two new absorption bands in the infrared spectrum at 1750 and 1700 cm^{-1} characteristic of bridging carbonyl groups. The final product from this decomposition showed the absence of any infrared bands which are characteristic of carbonyl groups.

The above evidence shows that the white compound formed at low temperatures is indeed $Ni(CO)_2$(*cis*-edas), analogous to the complex with *o*-phenylenebis(dimethylarsine). The major structural difference between the two ligands is the presence of an olefinic double bond in *cis*-1,2-bis(dimethylarsino)ethylene rather than an aromatic ring. Since more than two carbon monoxide groups are displaced by one *cis*-1,2-bis(dimethylarsino)ethylene ligand, the olefinic double bond must also be capable of coordinating to the nickel. Cullen[13] has observed the same complication in the reaction between 1,2-bis(dimethylarsino)tetrafluorocyclobutene and nickel carbonyl A recent structural investigation of an iron derivative of 1,2-bis(dimethylarsino)tetrafluorocyclobutene has shown that the olefinic double bond is indeed coordinated to the metal.[14]

Several attempts were made to prepare the *cis*-1,2-bis(dimethylarsino)ethylene derivatives of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$. The materials obtained from these reactions were complex mixtures containing bridging carbonyl and nitrosyl groups which were not further characterized. However, the *o*-phenylenebis(dimethylarsine) derivatives of the iron and cobalt nitrosyls were readily prepared. The nitrosyl complexes $Fe(NO)_2$(das) and Co(CO)(NO)(das) are reasonably stable in tetrahydrofuran and other ethers when air is exluded but are surprisingly unstable in hydrocarbon solvents such as hexane. The nitrosyl derivatives of iron and cobalt are much less stable than $Ni(CO)_2$(das) but were readily characterized by their infrared spectra and mass spectra. The parent molecular ions of all three compounds $Ni(CO)_2$(das), Co(CO)(NO)(das), and $Fe(NO)_2$(das) were observed but were among the weaker ions in the spectra. The mass spectra of $Fe(NO)_2$(das) and $Ni(CO)_2$(das) both contained ions in which one and two nitrosyl or carbonyl groups had been lost from the parent ion, but by far the most abundant ions were those due to the ligand *o*-phenylenebis(dimethylarsine) itself. The parent ion of the cobalt complex can fragment by losing either a carbonyl group or a nitrosyl group initially. Mass

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[12] B. J. Plankey and J. V. Rund, private communication.

[13] Footnote *c* of Table I.

[14] F. W. B. Einstein and J. Trotter, *J. Chem. Soc. A*, 832 (1967).

Table III

Prominent Ions in the Mass Spectra of *cis*-1,2-Bis(dimethylarsino)ethylene and *o*-Phenylenebis(dimethylarsine) Complexes

cis-edas		
m/e	Rel intens	Ions
236	96	$C_6H_{14}As_2$
221	100	$C_5H_{11}As_2$
210	9	$C_4H_{11}As_2$
195	76	$C_3H_9As_2$
180	6	$C_2H_6As_2$
165	2	CH_3As_2
151	16	HAs_2
140	19	C_5H_5As
125	21	C_4H_2As
105	52	C_2H_6As
90	13	CH_3As
75	4	As

$Cr(CO)_4$(*cis*-edas)		
m/e	Rel intens	Ions
400	28	$C_{10}H_{14}As_2O_4Cr$
385	0.3	$C_9H_{11}As_2O_4Cr$
372	0.6	$C_9H_{14}As_2O_3Cr$
344	5.5	$C_8H_{14}As_2O_2Cr$
329	1.8	$C_7H_{11}As_2O_2Cr$
316	28	$C_7H_{14}As_2OCr$
301	33	$C_6H_{11}As_2OCr$
288	100	$C_6H_{14}As_2Cr$
273	3.6	$C_5H_{11}As_2Cr$
262	54	$(C_2H_8As_2Cr)$
246	17	$C_3H_8As_2Cr$
231	10	$C_2H_5As_2Cr$
216	8	CH_2As_2Cr
202	9	As_2Cr
157	21	CH_2AsOCr

$Mo(CO)_4$(*cis*-edas)		
m/e	Rel intens	Ions
446	73	$C_{10}H_{14}As_2O_4Mo$
418	62	$C_9H_{14}As_2O_3Mo$
390	46	$C_8H_{14}As_2O_2Mo$
362	46	$C_7H_{14}As_2OMo$
346	40	$C_6H_{10}As_2OMo$
334	42	$C_6H_{14}As_2Mo$
318	37	$C_5H_{14}As_2Mo$
302	100	$C_3H_2As_2OMo$ or $C_4H_6As_2Mo$
300	100	C_3As_2OMo or $C_4H_4As_2Mo$
287	37	$C_5H_6O_3AsMo$
276	52	CAs_2OMo
261	74	$CHAs_2Mo$
248	75	As_2Mo

$W(CO)_4$(*cis*-edas)		
m/e	Rel intens	Ions
532	76	$C_{10}H_{14}As_2O_4W$
504	53	$C_9H_{14}As_2O_3W$
489	4	$C_8H_{11}As_2O_3W$
476	49	$C_8H_{14}As_2O_2W$
461	6	$C_7H_{11}As_2O_2W$
448	26	$C_7H_{14}As_2OW$
432	32	$C_7H_{10}As_2OW$
420	64	$C_6H_{14}As_2W$
406	23	$C_5H_{11}As_2W$
Too complex to identify monoisotopic species		
334	25	As_2W
315	100	C_3H_5AsW

$Ni(CO)_2$(*cis*-edas)		
m/e	Rel intens	Ions
350	1	$C_8H_{14}As_2O_2Ni$
322	3	$C_7H_{14}As_2ONi$
320	3	$C_6H_8As_2Ni$
294	4	$C_6H_{14}As_2Ni$
278	3	$C_5H_{10}As_2Ni$
277	3	$C_5H_9As_2Ni$
268	3	$(C_3H_8As_2ONi)$
262	90	$C_4H_6As_2Ni$
236	100	$C_6H_{14}As_2$

das		
m/e	Rel intens	Ions
286	16	$C_{10}H_{16}As_2$
271	100	$C_9H_{13}As_2$
256	57	$C_8H_{10}As_2$
241	7	$C_7H_7As_2$
227	8	$C_6H_5As_2$
226	5	$C_6H_4As_2$
182	8	$C_2H_8As_2$ or $C_8H_{11}As$
167	14	CH_5As_2 or C_7H_8As
165	5	CH_3As_2 or C_7H_6As
152	6	As_2H_2 or C_6H_5As
105	6	C_2H_6As
91	6	CH_4As
89	7	CH_2As
77	6	AsH or C_6H_5

$Mo(CO)_4$(das)		
m/e	Rel intens	Ions
496	30	$C_{14}H_{16}As_2O_4Mo$
468	55	$C_{13}H_{16}As_2O_3Mo$
453	6	$C_{12}H_{13}As_2O_3Mo$
440	56	$C_{12}H_{16}As_2O_2Mo$
425	13	$C_{11}H_{13}As_2O_2Mo$
412	22	$C_{11}H_{16}As_2OMo$
396	32	$C_{10}H_{12}As_2OMo$
384	100	$C_{10}H_{16}As_2Mo$
368	22	$C_9H_{12}As_2Mo$
350	37	$C_8H_6As_2Mo$
337	80	$C_7H_5As_2Mo$
324	45	$C_6H_4As_2Mo$
271	40	$C_9H_{13}As_2$
261	53	C_7H_4AsMo
248	62	As_2Mo
185	53	CAsMo
174	47	HAsMo

$Fe(NO)_2$(das)		
m/e	Rel intens	Ions
402	3	$C_{10}H_{16}As_2N_2O_2Fe$
372	5	$C_{10}H_{16}As_2NOFe$
357	0.3	$C_9H_{16}As_2NOFe$
342	0.3	$C_{10}H_{16}As_2Fe$
326	2	$C_9H_{12}As_2Fe$
286	19	$C_{10}H_{16}As_2$
271	100	$C_9H_{13}As_2$
256	70	$C_8H_{10}As_2$
241	8	$C_7H_7As_2$
226	7	$C_6H_4As_2$
182	2	$C_2H_8As_2$ or $C_8H_{11}As$
167	6	CH_5As_2 or C_7H_8As
165	4	CH_3As_2 or C_7H_6As
163	22	$CHAs_2$ or C_7H_4As
151	3	HAs_2 or C_6H_4As
125	8	C_4H_2As
105	4	C_2H_6As

Co(CO)(NO)(das)		
m/e	Rel intens	Ions
403	7	$C_{11}H_{16}As_2NO_2Co$
375	40	$C_{10}H_{16}As_2NOCo$
373	5	$C_{11}H_{16}As_2OCo$
360	10	$C_9H_{13}As_2NOCo$
348	0.7	$C_{10}H_{13}As_2OCo$
345	25	$C_{10}H_{16}As_2Co$
333	2	$C_9H_{10}As_2OCo$
329	8	$C_{10}H_{12}As_2Co$
315	2	$C_8H_{10}As_2Co$
301	3	$C_7H_8As_2Co$
299	3	$C_7H_6As_2Co$
298	3	$C_7H_4As_2Co$
286	37	$C_{10}H_{16}As_2$
271	100	$C_9H_{13}As_2$
256	60	$C_8H_{10}As_2$
244	20	$C_7H_{10}As_2$
241	8	$C_7H_7As_2$
239	5	As_2NOCo

$Ni(CO)_2$(das)		
m/e	Rel intens	Ions
400	0.4	$C_{12}H_{16}As_2O_2Ni$
372	8	$C_{11}H_{16}As_2ONi$
344	2	$C_{10}H_{16}As_2Ni$
329	4	$C_9H_{13}As_2Ni$
314	3	$C_8H_{10}As_2Ni$
299	2	$C_7H_7As_2Ni$
297	4	$C_7H_5As_2Ni$
286	3	$C_{10}H_{16}As_2$
271	100	$C_9H_{13}As_2$
256	83	$C_8H_{10}As_2$
241	16	$C_7H_7As_2$
227	16	$C_6H_5As_2$
210	5	H_2As_2Ni
208	5	As_2Ni

peaks identified as P − CO (*m/e* 375) and P − NO (*m/e* 373) were both observed, but the ion P − CO was present in much greater abundance (8:1) than the ion P − NO. Thus, the carbonyl group is much more readily lost from the parent ion than is the nitrosyl group, as is usually found in mixed carbonyl–nitrosyl complexes. The preferential loss of carbonyl groups is also a common feature in the chemical reactions of mixed carbonyl–nitrosyl complexes. The reactions described above are typical: when other ligands such as tertiary phosphines or arsines react with complexes containing both nitrosyl and carbonyl groups, carbon monoxide is almost always the ligand which is displaced. Exchange reactions between carbon monoxide have been studied and the rates of exchange are rather rapid. However, the exchange between nitric oxide and the nitrosyl group is very much slower, if it takes place at all.[15,16] These facts all point to the conclusion that the metal–nitrogen bond in nitrosyls is substantially stronger than the metal–carbon bond in metal carbonyls. Infrared studies also show that the metal–nitrogen force constants are greater than metal–carbon force constants in this class of compounds.[17]

The infrared spectra of these complexes were obtained, and the carbonyl and/or nitrosyl frequencies are listed in Table IV. The decrease in the stretching frequencies of the carbonyl and nitrosyl groups indicate that there is a substantial increase in the π bonding between the metal and the carbonyl or nitrosyl group on replacement of CO groups by the arsine ligand.

TABLE IV
INFRARED SPECTRAL DATA FOR DISUBSTITUTED DERIVATIVES OF $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, AND $Ni(CO)_4$

Compd	Str freq, cm^{-1}	Ref
$Fe(NO)_2(das)$	1716 (NO), 1660 (NO)	*a*
$Fe(NO)_2[As(C_6H_5)_3]_2$	1732 (NO), 1690 (NO)	*b*
$Co(CO)(NO)(das)$	1940 (CO), 1710 (NO)	*a*
$Co(CO)(NO)[P(C_6H_5)_3]_2$	1957 (CO), 1717 (NO)	*c*
$Ni(CO)_2(das)$	1996 (CO), 1931 (CO)	*d*
$Ni(CO)_2$(*cis*-edas)	2000 (CO), 1935 (CO)	*a*

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Racemization and Oxygen-18 Exchange Studies of Heterochelate Chromium(III) Complexes. II. The Cations Oxalatobis(2,2′-bipyridine)chromium(III), Oxalatobis(1,10-phenanthroline)chromium(III), and Oxalatobis(ethylenediamine)chromium(III)

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The kinetics of racemization and oxygen-18 exchange for $Cr(ox)bipy_2^+$, $Cr(ox)(phen)_2^+$, and $Cr(ox)(en)_2^+$ (where ox = oxalate ion, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been studied in acid solution. Racemization of $Cr(ox)(bipy)_2^+$ is markedly acid dependent whereas $Cr(ox)(phen)_2^+$ shows little acid dependence. Both complexes show distinct racemization rate dependences on addition of various anions or cations. An intramolecular racemization mechanism accounts for the overall behavior. The $Cr(ox)(en)_2^+$ complex is hydrolyzed readily in acid media and this contributes largely to loss of optical activity. All three cationic complexes show acid-catalyzed exchange of all their oxalate oxygens with solvent water. The four oxalate oxygens are kinetically indistinguishable. The exchange reactions are uniformly first order in acid and in complex. Arrhenius parameters for oxygen exchange and for racemization have been measured. Two mechanisms for oxygen exchange are consistent with the data and involve either oxalate ring opening or rapid carbonyl–carboxyl oxygen interchange.

Introduction

In a previous paper[2] we described racemization and oxygen-18 exchange behavior for anionic chromium(III) complexes as part of a systematic study on metal–oxalate complexes. In this paper we give results of work with the cationic complexes $Cr(ox)(bipy)_2^+$ and $Cr(ox)(phen)_2^+$ (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, ox = oxalate ion) together with a reinvestigation of $Cr(ox)(en)_2^+$ (en = ethylenediamine).

Some preliminary findings on oxygen-18 exchange have been published.[3] Werner[4] first reported that $Cr(ox)(en)_2^+$ racemized in aqueous solution and Bushra and Johnson[5] subsequently ascribed the rotation loss to

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