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2-METHYL-2-NITROSOPROPANE AND NITROSOBENZENE AS NITROGEN-BONDED PLATINUM(II) LIGANDS. MOLECULAR STRUCTURE OF $\{PtCl_2[(CH_3)_3C(NO)]_2\}$ *

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Summary

Two series of 2-methyl-2-nitrosopropane and nitrosobenzene complexes of platinum(II) have been synthesized including: $\{PtCl_3[(CH_3)_3C(NO)]\}^-K^+$ (I), $[PtCl_3(C_6H_5NO)]^-K^+$ (II); various *trans*-$\{PtCl_2[(CH_3)_3C(NO)]L\}$ complexes with L = various pyridines (III (Z)), nitrosobenzene (IV), and 2-methyl-2-nitrosopropane (V); various *trans*-$[PtCl_2(C_6H_5NO)L]$ complexes with L = various pyridines (VI (Z)) and nitrosobenzene (VII); *trans* and *cis* isomers of $[PtCl_2(C_6H_5NO)(PR_3)]$ complexes (VIII—XI). The X-ray structure of V, which is the first determined for a platinum(II)—nitrosoalkane complex, establishes its *trans* configuration and the *N*-coordination of 2-methyl-2-nitrosopropane to the metal. In complexes III (Z), change from 2,4,6-trimethyl- to 4-nitro-pyridine increases the N—O bond strength of 2-methyl-2-nitrosopropane, but this is not significant in the case of the nitrosobenzene complexes VI (Z).

Both X-ray and IR data favour nitrosoalkyl- and nitrosoaryl-platinum rather than platinum nitroxide structures and imply a small back donation from platinum(II) to the nitroso ligands. The nitroso compounds appear to have a π-accepting ability smaller than that of ethylene and larger than that of the pyridines.

Introduction

We recently showed that unstable nitrosoalkanes, in which the nitroso group is isoelectronic with dioxygen, are good ligands for hemoproteiniron(II) com-

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* No reprints available.

pounds [1—3], and synthesized model (porphyrin)(RNO)iron(II) complexes [4].

Several transition metal complexes of nitrosoarenes have been described, and exhibit various binding modes for the nitroso ligand. Oxygen binding probably occurs with nitrosobenzene bearing strongly electron donating amino groups at the *para* position, when it is coordinated to nickel(II), cobalt(II), copper(II), and zinc(II) [5]. Side-on η^5 coordination of the N=O group has been established for a nitrosobenzene derivative bridging the two metal atoms of an iron(0) dinuclear complex [6]. This side-on bridging is also suggested for nitrosoarenes coordinated to nickel(0), palladium(0) and platinum(0), and has been confirmed in the case of a trinuclear palladium(0) complex [7]. Nitrogen binding is the most common, and in the case of nitrosoarenes it has been confirmed for *trans*-$[PdCl_2(C_6H_5NO)_2]$ [8] and is strongly indicated by spectroscopic data for ruthenium(II)— [9] and iron(II)—phthalocyanine [10] complexes.

Few transition metal complexes of nitrosoalkanes have been described. A side-on η^2 coordination was proposed for nitrosomethane bridging the two metal atoms of a cobalt(I) dinuclear complex [11]. For chelate nitrosoalkyl ligands, nitrogen coordination was established in the case of a cobalt(I) bidentate dinitrosoalkyl complex [12], and a tris(violurato)iron(II) complex [13], and is very probable for a tris(3-nitroso-2,4-pentanedionato)cobalt(III) complex [14]. For monodentate nitrosoalkyl ligands one ruthenium(II) complex $\{Ru^{II}(NH_3)_5[HOC(CH_3)_2CH_2NO]\}^{2+}$ [15] has been described in addition to our (porphyrin)(RNO)iron(II) complexes [4] and some spectroscopic data are available for one ruthenium(II) * and some ferrocyanide [17,18] complexes.

In the case of the hemoproteins we observed that the nitrosoalkanes give much more stable iron(II) complexes than the nitrosoarenes [19]. This observation and the sparsity of data on nitrosoalkyl ligands, prompted us to investigate the ligand properties of 2-methyl-2-nitrosopropane and compare them with those of nitrosobenzene for a series of complexes of platinum(II), a metal for which *trans*-effects and *trans*-influences have been thoroughly classified [20]. We describe a study of 2-methyl-2-nitrosopropane- and nitrosobenzene-platinum(II) complexes, and present spectral data and an X-ray analysis, establishing the *N*-coordination of the nitroso ligands and a nitroso rather than a nitroxide structure for the complexes. The stabilities and configurations of the various complexes are discussed in the context of the nature of the other ligands.

Results

2-Methyl-2-nitrosopropane reacts stoichiometrically with K_2PtCl_4 in 50% acetone—water to give a 68% yield of $\{PtCl_3[(CH_3)_3C(NO)]\}^-K^+$ (I) after 24 h. Under the same conditions nitrosobenzene gives mainly *trans*-$[PtCl_2(C_6H_5NO)_2]$ (VII) and $[PtCl_3(C_6H_5NO)]^-K^+$ (II) in only 20% yield. The bis-nitroso ligand complexes *trans*-$\{PtCl_2[(CH_3)_3C(NO)]_2\}$ (V) and complex VII can be prepared in 80 and 75% yield, respectively, by reaction of K_2PtCl_4 with two moles of the

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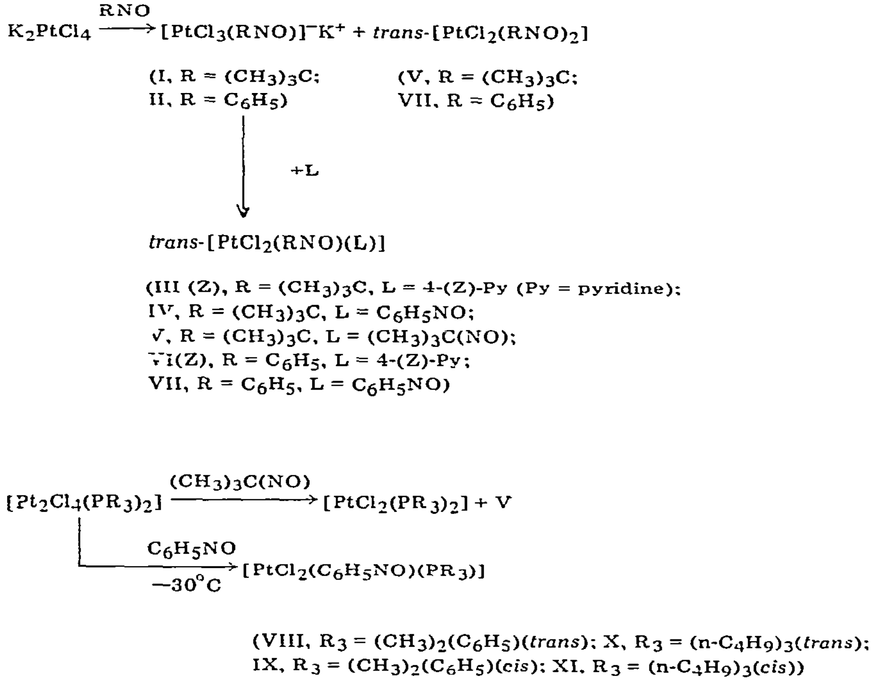
* An *N*-bound oximato form of the $CH_3COCH(NO)COCH_3$ ligand is actually postulated but the nitroso-dione complex cannot be excluded [16].

corresponding nitroso compound in the biphasic system chloroform/water (for V) or acetone/water (for VII) (Scheme 1).

SCHEME 1. 2-Methyl-2-nitrosopropane and nitrosobenzene complexes of platinum(II) and their preparations.



$$K_2PtCl_4 \xrightarrow{RNO} [PtCl_3(RNO)]^-K^+ + trans\text{-}[PtCl_2(RNO)_2]$$

(I, R = $(CH_3)_3C$; II, R = C_6H_5) (V, R = $(CH_3)_3C$; VII, R = C_6H_5)

$$\big\downarrow{+L}$$

trans-$[PtCl_2(RNO)(L)]$

(III (Z), R = $(CH_3)_3C$, L = 4-(Z)-Py (Py = pyridine);
IV, R = $(CH_3)_3C$, L = C_6H_5NO;
V, R = $(CH_3)_3C$, L = $(CH_3)_3C(NO)$;
VI(Z), R = C_6H_5, L = 4-(Z)-Py;
VII, R = C_6H_5, L = C_6H_5NO)

$$[Pt_2Cl_4(PR_3)_2] \xrightarrow{(CH_3)_3C(NO)} [PtCl_2(PR_3)_2] + V$$

$$[Pt_2Cl_4(PR_3)_2] \xrightarrow[-30^\circ C]{C_6H_5NO} [PtCl_2(C_6H_5NO)(PR_3)]$$

(VIII, $R_3 = (CH_3)_2(C_6H_5)$(*trans*); X, $R_3 = (n\text{-}C_4H_9)_3$(*trans*);
IX, $R_3 = (CH_3)_2(C_6H_5)$(*cis*); XI, $R_3 = (n\text{-}C_4H_9)_3$(*cis*))

When the salts I or II are suspended in chloroform they react quantitatively during 24 h with various pyridines to give the complexes III (Z) and VI (Z). The salts I and II also react, though more slowly, with the appropriate nitroso ligand to give the complexes V and VII, respectively, in 80 and 15% yield. The salt I and nitrosobenzene give the complex *trans*-$\{PtCl_2[(CH_3)_3C(NO)](C_6H_5NO)\}$ (IV) in 32% yield after two days. All the complexes gave correct elemental analyses (Table 6). The mass spectrometry (molecular ion and fragments) (Table 6), IR spectra (Tables 2 and 4) and ^{1}H NMR data (Tables 3 and 4) are in agreement with the proposed structures, the *trans* or *cis* configurations being assigned on the basis of IR and X-ray data (vide infra).

The X-ray structure of the bis(nitrosoalkyl) complex V establishes its *trans* configuration and shows that the nitrosoligands are *N*-coordinated (Fig. 1). The interatomic distances and angles are given in Table 1. The coordination plane and the plane containing the group O=N—C(1) are roughly perpendicular (87°). The conformation of the t-butyl group is shown in Fig. 2 which is represented as viewed down the N—C(1) bond. The length of that bond, 1.56(2) Å is outside the usual range for C—N single bonds (1.47 Å); comparison may be made with the large C—C (t-butyl) bonds found, for example, in 2,2-di-t-butyl-3,3-diphenylthiirane [21] or in tetra-t-butylacetone [22]. A better precision could not be obtained in the absence of absorption correction (see Experimental).

The IR spectra of the various $[PtCl_2(RNO)L]$ complexes (R = t-butyl or

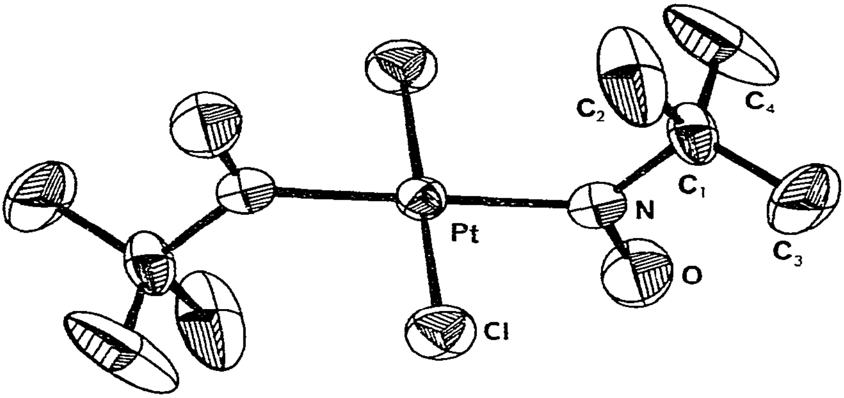


Fig. 1. Perspective drawing of complex V. The thermal ellipsoids are shown at the 50% probability level.

phenyl) (Table 2) all show a Pt—Cl ν_{as} vibration at ca. 350 cm^{-1}, which supports a *trans* configuration [23]. The great similarity between the ^{1}H NMR spectra of the various complexes within each of the 2-methyl-2-nitrosopropane and nitrosobenzene series (Table 3) is further evidence for their common *trans* configuration.

By comparing the IR spectra of the series of complexes *trans*-$\{PtCl_2[(CH_3)_3C(NO)]L\}$, particularly those containing substituted pyridines (Py), it is possible to assign the NO stretching band. All the complexes exhibit a band or doublet at 1363—1372 cm^{-1} and a band at 1392—1396 cm^{-1}, which are assigned to $\delta_s(CH_3)$, and also two bands at 1452, 1473 cm^{-1} which are assigned to $\delta_{as}(CH_3)$ [25]. The pyridine bands are identified by comparison with those of the corresponding free ligands and of several of their platinum complexes. The remaining band is tentatively assigned to ν(NO) (Table 2). The same comparison is made within the series of *trans*-$[PtCl_2(C_6H_5NO)L]$ complexes. All of them exhibit a band at 1487—1495 cm^{-1}, a band or doublet at 1460—1468 cm^{-1} and a band at 1434—1439 cm^{-1}. The same pattern is encountered for monomeric nitrosobenzene in diluted solution in $CHCl_3$: 1506, 1467, 1443 cm^{-1}, including the NO stretching frequency and the C—C skeletal modes. For monomeric nitrosobenzene the band at 1506 cm^{-1} has been assigned to ν(NO) [26]. Therefore we tentatively assign the band between 1487 and 1495 cm^{-1} to the ν(NO) stretch in the nitrosobenzene complexes (Table 2).

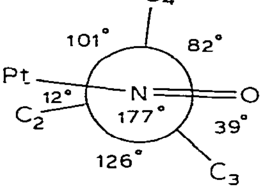


Fig. 2. The conformation of the t-butyl group in complex V crystals.

TABLE 1

INTERATOMIC DISTANCES AND ANGLES IN COMPLEX V (e.s.d. in parentheses)

Distances (Å)		Angles (°)	
Pt—Cl	2.295(3)	Cl—Pt—N	89.2(3)
Pt—N	1.967(9)	Pt—N—O	120(1)
N—O	1.21(1)	Pt—N—C(1)	124(1)
N—C(1)	1.56(2)	O—N—C(1)	116(1)
C(1)—C(2)	1.54(2)	N—C(1)—C(2)	109(1)
C(1)—C(3)	1.51(2)	N—C(1)—C(3)	111(1)
C(1)—C(4)	1.56(2)	N—C(1)—C(4)	102(1)

In order to synthesize complexes bearing a nitroso ligand and a phosphine, we first treated a suspension of the 2-methyl-2-nitrosopropane complex salt I in chloroform with triphenyl or tri-n-butyl phosphine. A reaction occurred at room temperature, and, with the former, the ^{1}H NMR spectrum showed two new t-butyl signals at 1.77 and 1.73 ppm. However, the work-up only gave the corresponding *cis*-$[PtCl_2(PR_3)_2]$ complexes and the bis-nitrosoalkyl complex V. The dimers $[Pt_2Cl_4(PR_3)_2]$ ($R_3 = (CH_3)_2(C_6H_5)$ or $(n\text{-}C_4H_9)_3$) react with two equivalents of 2-methyl-2-nitrosopropane at room temperature (but not at —30°C), but we could only isolate the corresponding *cis*-$[PtCl_2(PR_3)_2]$ and V complexes together with unchanged starting materials. The dimer $\{Pt_2Cl_4[P(CH_3)_2(C_6H_5)]_2\}$ reacts immediately with nitrosobenzene in chloroform at —30°C. Precipitation with hexane at —30°C gives the *trans* complex VIII in 95% yield. At room temperature a mixture of the *cis* and *trans* isomers is obtained.

TABLE 2

INFRARED N—O AND Pt—Cl STRETCHING FREQUENCIES (cm^{-1}) OF THE COMPLEXES *trans*-$\{PtCl_2[(CH_3)_3C(NO)]L\}$ AND *trans*-$[PtCl_2(C_6H_5NO)L]$

Nitroso ligand	L	Complex	ν(N—O) [a]	ν(Pt—Cl)
$(CH_3)_3C(NO)$	$(CH_3)_3$Py [b, c]	III $(CH_3)_3$	1498(1500)	348—332 [d]
	Cl	I	1528	340—334(sh), 319—307(sh) [e]
	4-CH_3Py	III (CH_3)	1532(1536)	348
	Py	III (H)	1536(1540)	348
	4-CNPy	III (CN)	1540(1544)	350
	4-NO_2Py	III (NO_2)	1550 [f] (1545)	354
	C_6H_5NO	IV	1554, (1557)	
			1502 [g] (1502) [g]	353
	$(CH_3)_3C(NO)$	V	1555(1557)	351
C_6H_5NO	4-CH_3Py	VI (CH_3)	1487(1495)	350
	Py	VI (H)	1489(1495)	352
	4-NO_2Py	VI (NO_2)	1491 [f] (1497)	347
	C_6H_5NO	VII	1494(1502)	350
	Cl	II	1495	342—332(sh), 319—309(sh) [e]

[a] KBr pellet; the $CHCl_3$ solution data are in parentheses. [b] Py = pyridine. [c] $(CH_3)_3$Py = 2,4,6-trimethylpyridine. [d] Such asymmetric bands or doublets are frequently observed for *trans*-$[PtCl_2$(olefin)(pyridine)$]$ complexes [24]. [e] (sh), shoulder. [f] $\nu(NO_2)_{as}$ 1354 cm^{-1}; $\nu(NO_2)_s$ 1536 cm^{-1}. [g] For C_6H_5NO.

TABLE 3

^{1}H NMR DATA FOR THE COMPLEXES *trans*-{$PtCl_2[(CH_3)_3C(NO)]L$} AND *trans*-[$PtCl_2(C_6H_5NO)L$][a]

Nitroso ligand	L	complex	$(CH_3)_3C(NO)CH_3$	C_6H_5NO			L = Py				
				o-H	*m*-H	*p*-H	*o*-H	*m*-H	*p*-H	*o*-CH_3	*p*-CH_3
$(CH_3)_3C(NO)$	Cl[b]	I	1.70								
	$(CH_3)_3Py$	III $(CH_3)_3$	1.70					6.93 (12)		3.27 (15)	2.33
	4-CH_3Py	III (CH_3)	1.75				8.44 (30)	7.12			2.40
	Py	III (H)	1.77				8.63 (31.5)	7.30	7.75		
	4-CNPy	III (CN)	1.77				8.93 (31.5)	7.56			
	4-NO_2Py	III (NO_2)	1.77				9.07 (31.5)	8.03			
	C_6H_5NO	IV	1.77	8.65	7.63	7.97					
	$(CH_3)_3C(NO)$	V	1.80								
C_6H_5NO	Cl[b]	II		8.65	7.67	7.98					
	4-CH_3Py	VI (CH_3)		8.63	7.57	7.88	8.57 (31.5)	7.17			2.47
	Py	VI (H)		8.63	7.50	7.74	8.72 (31.5)	7.34	7.74		
	4-NO_2Py	VI (NO_2)		8.63	7.57	7.88	9.20 (33)	8.07			
	C_6H_5NO[c]	VII		8.74	7.69	8.00					

[a] In $CDCl_3$ at 34°C, Varian EM 390; δ (ppm) from TMS (±0.02); $J(Pt—H)$ in Hz in parentheses. [b] In CD_3COCD_3. [c] Slightly soluble in $CDCl_3$, Bruker WH 90, Fourier transform 16 500 scans.

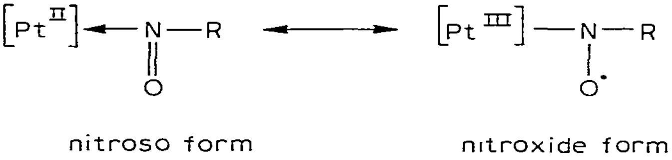
After a 24 h reaction at 50°C, precipitation with petroleum ether gives the *cis* complex IX in 92% yield. The *trans* and *cis* configurations are assigned on the basis of the Pt—Cl vibrations (Table 4). From the same reaction starting with the dimer $\{Pt_2Cl_4[P(n\text{-}C_4H_9)_3]_2\}$ in chloroform at —30°C, we could not precipitate the *trans* complex X, which is too soluble. A very slow precipitation in the cold gives another complex XI. Complex XI can be isolated after a 24 h reaction at 50°C in 35% yield. An X ray structure determination was performed with partial (the n-butyl chains being disordered) but sufficient refinement to establish the *N*-coordination of nitrosobenzene and the *cis*-configuration of complex XI. This configurational assignment is in agreement with the spectroscopic data (Table 4).

We also tried to synthesize complexes bearing a nitroso ligand and ethylene. When 2-methyl-2-nitrosopropane was tested with the dimer $[Pt_2Cl_4(C_2H_4)_2]$ in chloroform, the ^1H NMR spectrum (Varian EM 390 and Cameca 250 MHz, tetrachloroethane as internal standard, δ(ppm) from TMS), showed that the complex *trans*-$\{PtCl_2(C_2H_4)[(CH_3)_3C(NO)]\}$ was the primary product of the chloro-bridges cleavage (coordinated C_2H_4 in fast exchange with free C_2H_4: singlet, δ changing from 5.10 to 4.80 ppm) and that this was then transformed at room temperature into the *cis* isomer (C_2H_4: triplet, δ 4.45 ppm, *J*(Pt—H) 66 Hz) *. The latter is also unstable under these conditions, and complex V (which can be isolated by preparative thin layer chromatography in 30% yield) is formed together with other complexes which will be described in a later paper. The same type of multistep reaction occurs with nitrosobenzene.

Discussion

2-Methyl-2-nitrosopropane and nitrosobenzene must be added to the list of ligands (L) which give $[PtCl_3L]^-$ complexes: viz. L = C_2H_4, CO, NO, PR_3, AsR_3, SR_2, NH_3, pyridine, and DMSO [28—30]. It is noteworthy that the salts I and II can be obtained directly from K_2PtCl_4 at room temperature, and that this is a good method of preparation for complex I.

In the light of the electronic structure of the N=O group of the nitroso ligands, which is isoelectronic with dioxygen, it is of interest to investigate the respective contributions of the two following resonance forms to the metal—nitroso compound bond:



$$[Pt^{II}] \leftarrow \underset{\overset{\|}{O}}{N} - R \longleftrightarrow [Pt^{III}] - \underset{\overset{|}{O^{\bullet}}}{N} - R$$

The main structural features of complex V are compared in Table 5 with those reported for *trans*-$[PdCl_2(C_6H_5NO)_2]$ [8] and for the dinitrosoalkylcobalt chelate complex: bicyclo[2.2.1]hept-2-en-5,6-dinitrosocobalt-η^5-cyclopentadienide [12].

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* This attribution is based on a comparison with the data relative to the ethylenic protons in various *cis*- and *trans*-$[PtCl_2(C_2H_4)(amine)]$ complexes, for these the chemical shift is larger for the *trans* isomer than for the *cis*, and the ^{195}Pt—H coupling constant is larger for the *cis* isomer than for the *trans* [27].

TABLE 4

SPECTROSCOPIC DATA FOR THE *trans* AND *cis* COMPLEXES [$PtCl_2(C_6H_5NO)(PR_3)$]

Complex		IR (cm^{-1})		^1H NMR (δ, ppm)				
		ν(NO) [a]	ν(Pt—Cl)	C_6H_5NO			$P(CH_3)_2(C_6H_5)$	
				o-H	*m*-H	*p*-H	^2J(P—H) (Hz)	^3J(Pt—H) (Hz)
VIII	$R_3 = (CH_3)_2(C_6H_5)$(*trans*)	1491	350—326(sh) [d]	8.67 [b]	7.68	7.91	12	31
IX	$R_3 = (CH_3)_2(C_6H_5)$(*cis*)	1486	348, 290	8.28 [c]	7.48	7.85	11.7	36
X	$R_3 = (n\text{-}C_4H_9)_3$(*trans*)			8.68 [b]	7.67	7.90		
XI	$R_3 = (n\text{-}C_4H_9)_3$(*cis*)	1484	340, 300	8.59 [c]	7.62	7.94		

[a] A pattern of three bands is observed as for the complexes II, VI (Z) and VII (Table 2), respectively, 1491, 1461 and 1436 for complex VIII, 1486, 1466 and 1432 for complex IX and 1484, 1463 and 1430 for complex XI; the tentative ν(NO) assignment is done similarly. [b] In $CDCl_3$ at −30°C, Cameca 250 MHz; δ in ppm from TMS. [c] In $CDCl_3$ at 34°C, Varian EM 390. [d] (sh) shoulder.

TABLE 5

COMPARISON OF THE X-RAY DATA FOR COMPLEX V WITH THOSE FOR TWO REPORTED PALLADIUM(II) AND COBALT(I) COMPLEXES

Complex	Bond lengths (Å)		Angles (°)			Reference
	M—N [a]	N—O	M—N—O	M—N—C [b]	O—N—C [b]	
trans-[$PdCl_2(C_6H_5NO)_2$]	1.994	1.209	118.7	122.9	118.2	8
$(C_5H_5)Co(C_7H_8N_2O_2)$	1.761	1.252	129.4	118.2	112.4	
	1.764	1.247	128.9	118.2	112.9	12
trans-$\{PtCl_2[(CH_3)_3C(NO)]_2\}$	1.967	1.21	120	124	116	This work

[a] M = metal. [b] C is the carbon atom bearing the NO group.

The structure of complex V is very similar to that of *trans*-[$PdCl_2(C_6H_5NO)_2$]. The N—O bond length is shorter than that in the cobalt(I) chelate complex. It is also shorter than the N—O bond (1.24 Å) of monomeric 4-iodonitrosobenzene, which must be longer than that of monomeric nitrosobenzene because electron donating by the iodo substituent stabilizes the monomeric species [31].

For the complex ion $\{Ru(NH_3)_5[HOC(CH_3)_2CH_2NO]\}^{2+}$, the 1370 and 1365 cm^{-1} bands have been assigned to the $\nu(NO)$ vibration by ^{15}N labeling [15]. The authors compared this NO stretch with that of *trans*-[$PdCl_2(C_6H_5NO)_2$], which they reported as "in the 1446 cm^{-1} region" *, and with the $\nu(NO)$ of di-t-butyl nitroxide either free (at 1343 cm^{-1}) or bound by its oxygen atom in the complex $\{Co[(CH_3)_3C)_2NO]_2Cl_2\}$ (at 1326 cm^{-1}) **. They concluded that their ruthenium complex could involve the contribution of both the ruthenium(II)—nitroso and the ruthenium(III)—nitroxide valence forms [15]. For the bicyclo[2.2.1]hept-2-en-5,6-dinitrosocobalt-η^5-cyclopentadienide complex, the NO stretching frequency is at 1357 cm^{-1} [34], and the N—O bond length is 1.252 Å. This has been interpreted as evidence for a coordinated nitroxyl diradical bidentate ligand [12]. For the nitrosoarene complexes $\{Ru(bipy)[R(CH_3)NC_6H_4NO]Cl\}PF_6$, ^{15}N labeling led to the assignment of the bound NO stretching vibrations to the 1284 cm^{-1} ($R = H$) and 1286 cm^{-1} ($R = CH_3$) bands. This considered along with other spectral and electrochemical data has been interpreted as a consequence of extensive π-back bonding from ruthenium(II) to the nitrosoarene ligands [9].

In the case of the 2-methyl-2-nitrosopropane and nitrosobenzene complexes studied, the $\nu(NO)$ frequencies observed are close to those of the corresponding free monomeric ligands (1546 and 1506 cm^{-1}, respectively [26]). For the 2-methyl-2-nitrosopropane complexes III (Z) from Z = 2,4,6-$(CH_3)_3$ to 4-NO_2, the variation of the *trans* influence of the pyridinic ligand causes a 50 cm^{-1} increase of $\nu(NO)$ (Table 2), corresponding to an increase of the N—O bond strength. This effect is more pronounced on replacement of the pyridines by nitrosobenzene and 2-methyl-2-nitrosopropane, suggesting a larger π-accepting ability of the nitroso ligands than of 4-nitropyridine. A similar effect has been

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* Actually they refer to ref. 32 which gives the following list of IR absorptions 1579s, 1553(sh), 1496s, 1451m, 1432s, 1340w, 1318m without $\nu(NO)$ assignment.

** Ref. [25]. When bound through both N and O to palladium in $\{PdCl[((CH_3)_3C)_2NO]\}_2$, di-t-butyl nitroxide exhibits 1096 and 1022 cm^{-1} bands tentatively assigned to $\nu(NO)$ [33].

reported for *trans*-[$PtCl_2(CO)(4\text{-}Z\text{-}Py)$] complexes, for which the $\nu(CO)$ increase is of 15 cm^{-1} on change of Z from CH_3 to NO_2 [35,23]. The same comparison for the nitrosobenzene complexes VI (Z) does not show a significant variation of $\nu(NO)$ on change of the *trans*-pyridine (Table 2).

Both X-ray and IR data for the studied complexes are thus in favour of nitrosoalkylplatinum and nitrosoarylplatinum rather than platinum nitroxide structures. They also show that there is much less back donation to the nitroso ligands from platinum(II) than from ruthenium(II), cobalt(I) or iron(II) *.

We have not been able to isolate a {$PtCl_2[(CH_3)_3C(NO)](PR_3)$} complex, and the *trans*-[$PtCl_2(C_6H_5NO)(PR_3)$] complexes are easily isomerized to the *cis* isomers. Furthermore we have not been able to isolate any [$PtCl_2(C_2H_4)$-(RNO)] complex (with R = alkyl or phenyl), and could only get spectral evidence of the successive formation of the *trans* and *cis* isomers. The stability of the [$PtCl_2(RNO)(L)$] complexes decreases sharply with the increasing *trans*-effect of the L ligands, from pyridine to ethylene. A comparison of this trend with that for [$PtCl_2(Py)(L)$] complexes [27a] suggests a larger π-accepting ability for the nitroso ligands than for the pyridines, in agreement with the above IR data. However the stability of the *trans*-{$PtCl_2[(CH_3)_3C(NO)]_2$} complex, compared to that of *trans*-[$PtCl_2(C_2H_4)_2$] [36], is evidence for a smaller π-accepting ability of the nitroso ligands than of ethylene.

Experimental

The melting points are uncorrected. The IR spectra were recorded on a Perkin—Elmer Model 457 spectrometer and the ^1H NMR spectra on various machines as noted in the text or tables. The mass spectra were recorded with a Varian CH7 Model. Table 6 lists experimental data not presented in the text.

Preparation of the salts [$PtCl_3(RNO)]^-K^+$ (I, II) (Method a in Table 6)

To a 30 ml aqueous solution of 1 g K_2PtCl_4 (2.4×10^{-3} mol) is added 30 ml of an acetone solution of 2-methyl-2-nitrosopropane. The mixture is stirred at room temperature for 24 h, the solution becoming dark red. After evaporation of the solvent the water soluble products are separated, the aqueous solution is evaporated, and the salt I is dissolved in acetone and recrystallized from acetone/ ether. The same procedure was used for the preparation of complex II.

Preparation of the complexes [$PtCl_2(RNO)L$] (III (Z), IV, VI (Z)) (Method b in Table 6)

200 mg of the [$PtCl_3(RNO)]^-K^+$ salt are suspended in a 20 ml chloroform solution containing a stoichiometric amount of the L ligand, and the mixture is stirred for 24 h at room temperature (48 h for R = t-butyl and L = 2,4,6-trimethylpyridine and nitrosobenzene). After usual work-up the complexes are recrystallized from a concentrated chloroform solution by slow addition of hexane or petroleum ether.

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* IR data for the (iron(II))(tetraphenylporphyrin)(nitroso ligand) complexes reported in ref. 4, show that the $\nu(NO)$ of bound 2-nitrosopropane and nitrosomethane are at 1435 and 1405 cm^{-1} respectively with a *trans*-pyridine ligand, and that they vary as predicted with the σ- and π-properties of various *trans* ligands. Preliminary X-ray data for the N—O bond length are in agreement with these results (to be published).

Preparation of the complexes [$PtCl_2(RNO)_2$] (V, VII) (Method c in Table 6)

25 ml of an aqueous solution of 415 mg of K_2PtCl_4 (10^{-3} mol) are mixed with 25 ml of a chloroform solution of 174 mg of 2-methyl-2-nitrosopropane (2×10^{-3} mol) and the mixture is vigorously stirred for 7 days. After usual work up complex V is washed with petroleum ether and recrystallized from chloroform/ petroleum ether. The same procedure was used for complex VII, but with a 50% water/acetone mixture.

Preparation of the complexes [$PtCl_2(C_6H_5NO)(PR_3)$] (VIII, IX, XI) (Method d in Table 6)

Complex VIII. 150 mg of $\{Pt_2Cl_4[P(CH_3)_2(C_6H_5)]_2\}$ (18.6×10^{-3} mol) are dissolved in 10 ml of chloroform and the solution treated at —30°C with 40 mg of nitrosobenzene. After 30 min the complex VIII is precipitated with 100 ml of hexane at —30°C. The complex is recrystallized in the cold from chloroform/ hexane.

Complexes IX and XI. These complexes are obtained by the same procedure but at room temperature, and in better yields from reaction at 50°C.

Molecular structure of $\{PtCl_2[(CH_3)_3C(NO)]_2\}$ (V)

Crystal data. The crystals of the compound are dark-red prisms. A single crystal of about $0.3 \times 0.3 \times 0.35$ mm^3 was mounted on a glass fiber to be used both for the determination of the unit-cell and for the data collection. A least-squares refinement over 66 "high" reflections ($\sin \theta/\lambda > 0.24$), previously centered on a 4-circle diffractometer, using Mo-K_α (λ 0.71073 Å) radiation, gave the following unit-cell dimensions: a 12.973(3), b 11.062(3), and c 9.929(2) Å. The systematic absences ($0kl$, $k \neq 2n$, $h0l$, $l \neq 2n$, and $hk0$, $h \neq 2n$) are consistent with the orthorhombic space group *Pbca*.

The data were collected using the $\theta/2\theta$ multiple scan technique (up to 8 scans, depending on the intensity of each reflexion), with a speed of 0.25° s^{-1} and a constant scan width of 1.5°. The measurement of the background was performed during 15 s for both sides of every reflexion. From 2806 independent intensities ($2 < \theta < 33°$), only 924 were included in the data set, their value being greater than twice their rms deviation, calculated from counting statistics [37]. The Lorentz and the polarization corrections were applied, but none for absorption in spite of the high absorption coefficient (μ 107 cm^{-1}).

Structure determination and refinement. A rough estimate of the crystal density (1.9 by flotation in an aqueous mixture of KI and $ZnBr_2$), indicates the number of molecules in the cell to be 4. The platinum atoms are therefore located at inversion centers. The calculated density is 2.05. A Fourier synthesis revealed the positions of all non hydrogen atoms. The refinement was performed using the full-matrix method with the atomic scattering factors of the International Tables [38], including the anomalous scattering contributions for Pt and Cl. The quantity which was minimized is $\Sigma w(|F_0| - |F_c|)^2$, where $w = \sigma^{-2}$ is the weight [37] associated with each structure factor. Only the 910 reflexions with $5 < \theta < 33°$ were included in the last cycles of the anisotropic refinement. Table 7 gives the final values of the parameters. The discrepancy factor $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ is 0.038; the weighted R factor $\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2$ is 0.029.

TABLE 6

EXPERIMENTAL DATA FOR THE VARIOUS COMPLEXES SYNTHESIZED

Complexes	M.p. (°C)	Elemental analyses (Found (calcd.) (%))						M^+ [b]	Colour	Method	Yield (%)
		C	H	N	Cl	Pt	K or P				
I	170 [a]	10.99	2.07	2.93	24.46	45.50	9.23		red	a	68
		(11.32)	(2.12)	(3.27)	(24.87)	(45.62)	(9.14)				
II	125 [a]	16.06	1.11	3.08	23.67	42.47			red	a	20
		(16.10)	(1.13)	(3.13)	(23.76)	(43.56)	(8.73)		violet		
III ($(CH_3)_3$)	183	30.31	4.20	5.88	15.08			474	red	b	98
		(30.39)	(4.25)	(5.91)	(14.95)	(41.13)					
III (CH_3)	153	26.98	3.67	6.32	16.11	43.48		446	red	b	95
		(26.92)	(3.61)	(6.28)	(15.89)	(43.72)					
III (H)	150	25.02	3.28	6.40	16.39	44.57		432	red	b	96
		(25.01)	(3.26)	(6.48)	(16.40)	(45.14)					
III (CN)	159	26.28	2.84	9.17	16.11	42.17		457	red	b	93
		(26.27)	(2.87)	(9.19)	(15.51)	(42.67)					
III (NO_2)	180	22.57	2.67	8.80	14.91	40.56		477	red	b	90
		(22.65)	(2.75)	(8.80)	(14.86)	(40.88)					
IV	132	26.19	3.11	6.13	16.02	41.52		460	dark	b	32
		(26.10)	(3.07)	(6.09)	(15.41)	(42.39)			green		
V	157 [a]	21.50	4.21	6.18	16.34	43.77		440	dark	c	80
		(21.83)	(4.12)	(6.36)	(16.11)	(44.31)			red		
VI (CH_3)	222	30.99	2.60	6.02	15.13	41.09		466	green	b	98
		(30.91)	(2.59)	(6.01)	(15.21)	(41.84)					
VI (H)	210	29.22	2.25	6.20	15.88	43.14		452	green	b	98
		(29.22)	(2.23)	(6.19)	(15.68)	(43.14)					
VI (NO_2)	220	26.75	1.81	8.33	14.25	38.45		497	brown	b	98
		(26.57)	(1.82)	(8.45)	(14.26)	(39.24)			green		
VII	210 [a]	30.01	2.23	5.71	15.18	40.54		480	dark	c	75
		(30.01)	(2.10)	(5.83)	(14.76)	(40.62)			green		
VIII	108	32.16	3.11	2.63	14.59	38.12			dark	d	95
		(32.89)	(3.15)	(2.74)	(13.87)	(38.16)	(6.06)		green		
IX	167	32.80	3.24	2.58					red	d	92
		(32.89)	(3.15)	(2.74)	(13.87)	(38.16)	(6.06)				
XI	118	37.95	5.49	2.44	12.55		5.50	575	dark	d	35
		(37.57)	(5.61)	(2.43)	(12.32)	(33.90)	(5.38)		red		

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[a] With decomposition. [b] Mass spectra, Varian CH7, 70 eV, Temperature range 50—170°C, the mass of the molecular ion is given for the largest peak of the isotope cluster. The most frequent fragments are at m/e: $M - L$, $M - Cl$, $M - (L + Cl)$, $M - R$, $M - RNO$, $M - (RNO + Cl)$, with $R = (CH_3)_3$ or C_6H_5.

TABLE 7

ATOMIC COORDINATES FOR THE STRUCTURE OF COMPLEX V

(e.s.d. in parentheses)

	x/a	y/b	z/c
Pt	0.5	0.5	0.
Cl	0.5929(2)	0.6731(3)	0.0389(3)
N	0.4636(6)	0.4953(12)	0.1222(9)
O	0.5214(6)	0.4480(10)	0.2719(10)
C(1)	0.3653(9)	0.5550(11)	0.2538(13)
C(2)	0.3162(11)	0.6384(16)	0.1480(15)
C(3)	0.3896(13)	0.6175(18)	0.3855(15)
C(4)	0.2923(11)	0.4438(15)	0.2713(22)

cis-Configuration of the complex $\{PtCl_2(C_6H_5NO)[(n\text{-}C_4H_9)_3P]\}$ *(XI)*

The crystals of the complex are thin dark-red needles. The orthorhombic space group is *Pbcn*, $Z = 8$. The cell dimensions are: *a* 14.763, *b* 19.039 and *c* 16.610 Å. From Cu-K_α diffractometer data, 1365 non-zero intensities were used in a heavy-atom structure determination. The latter revealed the chlorine atoms to be in *cis* positions. Since the n-butyl chains are disordered no further refinement was performed once the structure of the complex was established (*R* 10.7%).

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References

1 D. Mansuy, P. Beaune, J.C. Chottard, J.F. Bartoli and P. Gans, Biochem. Pharmacol., 25 (1976) 609.
2 D. Mansuy, P. Gans, J.C. Chottard and J.F. Bartoli, Eur. J. Biochem., 76 (1977) 607.
3 D. Mansuy, J.C. Chottard and G. Chottard, Eur. J. Biochem., 76 (1977) 617.
4 D. Mansuy, P. Battioni, J.C. Chottard and M. Lange, J. Amer. Chem. Soc., 99 (1977) 6441.
5 C.J. Popp and R.O. Ragsdale, Inorg. Chem., 7 (1968) 1845; J. Chem. Soc. A, (1970) 1822.
6 M.J. Barrow and O.S. Mills, J. Chem. Soc., A, (1971) 864.
7 S. Otsuka, Y. Aotani, Y. Tatsuno and T. Yoshida, Inorg. Chem., 15 (1976) 656.
8 R.G. Little and R.J. Doedens, Inorg. Chem., 12 (1973) 537.
9 W.L. Bowden, W.F. Little and T.J. Meyer, J. Amer. Chem. Soc., 96 (1974) 5605; 97 (1975) 6897; 98 (1976) 444.
10 J.J. Watkins and A.L. Balch, Inorg. Chem., 14 (1975) 2720.
11 H.F. Klein and H.H. Karsch, Chem. Ber., 109 (1976) 1453.
12 G. Evrard, R. Thomas, B.R. Davis and I. Bernal, J. Organometal. Chem., 124 (1977) 59.
13 C.L. Raston and A.M. White, J. Chem. Soc. Dalton, (1976) 1915.
14 L.A. Epps, K. Wiener, R.C. Stewart and L.G. Marzilli, Inorg. Chem., 16 (1977) 2663.
15 J.N. Armor, R. Furman and M.Z. Hoffman, J. Amer. Chem. Soc., 97 (1975) 1737.
16 M. Mukaida, M. Yoneda and T. Nomura, Bull. Chem. Soc. Jap., 50 (1977) 3053.
17 W.A. Waters, J. Chem. Soc. Perkin II, (1976) 732.
18 A. Ishigaki, M. Oue, Y. Matsushita, I. Masuda and T. Shono, Bull. Chem. Soc. Jap., 50 (1977) 726.
19 D. Mansuy, P. Beaune, T. Cresteil, C. Bacot, J.C. Chottard and P. Gans, Eur. J. Biochem., in press.
20 U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London and New York, (1974), p. 44—50.

21 A. Mugnoli and M. Simonetta, Acta Cryst. B, 32 (1976) 1762.
22 G. Lepicard, J. Berthou, J. Delettré, A. Laurent and J.-P. Mornon, C.R. Acad. Sci. Paris, C, 276 (1973) 575.
23 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 14 (1975) 25.
24 J.C. Chottard, E. Mulliez, J.P. Girault and D. Mansuy, J. Chem. Soc. Chem. Commun., (1974) 780.
25 W. Beck, K. Schmidtner and H.J. Keller, Chem. Ber., 100 (1967) 503.
26 C.N.R. Rao and K.R. Bhaskar in H. Feuer (Ed.), The Chemistry of the Nitro and Nitroso Groups, Patai Series, Wiley Interscience, New York, 1969, 138.
27 (a) M. Orchin and P.J. Schmidt, Inorg. Chim. Acta Rev., 2 (1968) 123; (b) A. de Renzi, G. Paiaro and A. Panunzi, Gazz. Chim. Ital., 102 (1972) 413.
28 R.J. Goodfellow, P.L. Goggin and D.A. Duddell, J. Chem. Soc. A, (1968) 504, and ref. therein.
29 P.C. Kong and F.D. Rochon, J. Chem. Soc. Chem. Commun., (1975) 599 and ref. therein.
30 Y.N. Kukushkin, Y.E. Vyaz'menskii and L.I. Zorina, Russ. J. Inorg. Chem., 13 (1968) 1573.
31 M.S. Webster, J. Chem. Soc., (1956) 2841.
32 A.L. Balch and D. Petridis, Inorg. Chem., 8 (1969) 2247.
33 W. Beck and K. Schmidtner, Chem. Ber., 100 (1967) 3363.
34 H. Brunner and S. Loskot, Angew. Chem. Int. Ed., 10 (1971) 515.
35 M. Orchin and P.J. Schmidt, Inorg. Chim. Acta Rev., 2 (1968) 123.
36 Ref. 20, p. 359.
37 G.H. Stout and L.H. Jensen, X-ray Structure Determination, MacMillan, London, 1972, p. 456.
38 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.