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Coordination chemistry of NSO^-, NSO_2^- and S_3N^- ligands: comparison of electronic structure of Rh–NSO, Rh–SH and Rh–Cl complexes

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Abstract

$CsNSO_2$ reacts with fluoro complexes, *trans*-$[M(CO)F(PPh_3)_2]$ ($M = Rh$, Ir) to give sulfonylnitrido complexes, *trans*-$[M(CO)(NSO_2)(PPh_3)_2]$ which react with triphenylphosphine to afford thionitro complexes, *trans*-$[M(CO)(NSO)(PPh_3)_2]$. The thionitro complexes are also prepared by the reaction of $CsNSO_2$ with hydrido complexes, $[MH(CO)(PPh_3)_3]$. Reaction of $CsNSO_2$ with $[RuH_2(CO)(PPh_3)_2]$ yields $[Ru(CO)(NSO_2)_2(PPh_3)_2]$. The sulfonylnitrido complexes of the type $Cs_2[M'(NS)(NSO_2)_2Cl_3]$ ($M' = Ru$, Os) are prepared by the reaction of $CsNSO_2$ and $[M'(NS)Cl_3]$. The reactions of heptasulfurimide with $[RhCl(PPh_3)_3]$ and $[Rh(CO)Cl(PPh_3)_2]$ afford disulfidothinitrato complexes $[Rh(S_3N)(PPh_3)_2]$ and $[Rh(CO)(S_3N)(PPh_3)_2]$, respectively. CNDO/2 molecular orbital calculations have been performed on the model systems *trans*-$[Rh(CO)L(PH_3)_2]$ ($L = NSO$, SH, Cl) in order to investigate the nature and energetics of the interaction between rhodium and NSO, SH, Cl ligands. The computed trends for Rh–X, Rh–C and C–O bond strengths, as measured by Wiberg indices and charge distributions, suggest that the strength of the coordination bond Rh–L increases in the order [Rh–NSO] < [Rh–Cl] < [Rh–SH] and the strength of the Rh–C bond increases in the order $[Rh(CO)Cl(PH_3)_2] < [Rh(CO)(NSO)(PH_3)_2] < [Rh(CO)(SH)(PH_3)_2]$. The trend in C–O bond strength is $[Rh(CO)Cl(PH_3)_2] > [Rh(CO)(NSO)(PH_3)_2] > [Rh(CO)(SH)(PH_3)_2]$. The NSO group is the worst π-acceptor amongst the three ligands.

Introduction

Although the synthesis of transition metal thionitro complexes (M–NSO) has been a subject of much current activity [1–8], there is no report of a M–NSO_2 complex so far. Transition metal disulfidothionitrate complexes are an important and rapidly growing class of cyclometallothiazenes. These complexes have been prepared by the reaction of S_4N_4, S_3N^- salts or S_7NH with metal salts or metal complexes [9–14]. Herein is reported: (a) the synthesis and spectral studies of coordinated compounds of NSO^-, NSO_2^- and S_3N^- ligands, and (b) CNDO/2 molecular orbital calculations on the model compounds *trans*-$[Rh(CO)L(PH_3)_2]$ ($L = NSO$, SH, Cl).

Experimental

All the reagents used were AnalaR or of chemically pure grade. The solvents were dried, freshly distilled and degassed with nitrogen gas before use. The products are highly air and moisture sensitive, therefore the reactions were performed in Schlenk apparatus under a pure and dry nitrogen atmosphere.

Cesium sulfonylnitride, heptasulfurimide, fluorocarbonylbis(triphenylphosphine)rhodium(I), fluorocarbonylbis(triphenylphosphine)iridium(I), hydridocarbonyltris(triphenylphosphine)rhodium(I), hydridocarbonyltris(triphenylphosphine)iridium(I), dihydridocarbonyltris(triphenylphosphine)ruthenium(II), chlorotris(triphenylphosphine)rhodium(I), chlorocarbonylbis(triphenylphosphine)rhodium(I), thionitrosylrutheniumtrichloride and thionitrosylosmiumtrichloride were prepared by the literature methods [15–24].

Analysis

Carbon, hydrogen and nitrogen analyses were performed by Beller in Göttingen, F.R.G. and by the microanalytical section of the Indian Institute of Technology, Kanpur, India. Estimations of chloride and sulfur were carried out from the decomposed solution of the complexes by standard methods [25]. The IR spectra of the samples were recorded with Perkin-Elmer model 580 and model 735 B spec-

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TABLE 1. Analytical data of complexes

Complex	Found (calc.) (%)				
	C	H	N	S	Cl
$[Rh(CO)(NSO_2)(PPh_3)_2]$	60.5	4.1	2.0	4.5	
	(60.57)	(4.09)	(1.91)	(4.36)	
$[Ir(CO)(NSO_2)(PPh_3)_2]$	53.9	3.8	1.9	4.0	
	(54.01)	(3.61)	(1.70)	(3.89)	
$[Ru(CO)(NSO_2)_2(PPh_3)_2]$	54.7	3.9	3.5	7.8	
	(54.88)	(3.70)	(3.46)	(7.91)	
$[Cs_2[Ru(NS)(NSO_2)_2Cl_3]$			10.0	23.5	26.3
			(10.25)	(23.44)	(26.00)
$Cs_2[Os(NS)(NSO_2)_2Cl_3]$			8.4	19.4	21.6
			(8.42)	(19.25)	(21.36)
$[Rh(CO)(NSO)(PPh_3)_2]$	61.8	4.0	2.2	4.6	
	(61.92)	(4.18)	(1.95)	(4.46)	
$[Ir(CO)(NSO)(PPh_3)_2]$	55.2	3.8	1.9	4.1	
	(55.08)	(3.72)	(1.73)	(3.97)	
$[Rh(S_3N)(PPh_3)_2]$	58.4	4.1	1.7	13.2	
	(58.61)	(4.07)	(1.90)	(13.05)	
$[Rh(CO)(S_3N)(PPh_3)]$	45.3	3.1	2.5	19.2	
	(45.33)	(2.98)	(2.78)	(19.08)	

trometers in the range 4000–250 cm^{-1}; samples were prepared as CsI pellets. The mass spectra of some of the complexes were recorded by Dr Böhler, Göttingen, F.R.G. Analytical data and important IR frequencies of the complexes are given in Tables 1 and 2.

Computational details

Molecular orbital calculations were done using the CNDO/2-U method [26]. The orbitals 4d, 5s and 5p of rhodium were included in the calculations. Wave functions for these orbitals were those given by Burns [27]. The wave functions used for Cl(3s and 3p), S(3s and 3p), P(3s and 3p), N(2s and 2p), C(2s and 2p) and H(1s) were Slater type orbitals. The values for the orbital exponent, beta and electronegativities [28] are listed in Table 3. Atomic charges and bond overlap populations were obtained by Mulliken population analysis [29]. The coordinate system for square planar rhodium complexes is given in Fig. 1. Interatomic distances and bond angles, used for model systems, were taken from X-ray diffraction measurements for *trans*-$[Rh(CO)(NSO)Cl(PPh_3)_2]$ [4], *trans*-$[Rh(CO)(SH)(PPh_3)_2]$ [30] and *trans*-$[Rh(CO)Cl(PPh_3)_2]$ [31]. These complexes contain the L ligand (L = NSO, SH, Cl) *trans* to the CO group as deduced from X-ray crystal structure determination of the complexes [4, 30, 31]. The ^{31}P NMR spectrum of *trans*-$[Rh(CO)(SH)(PPh_3)_2]$ exhibits a doublet at 36.2 ($J(^{103}Rh-^{31}P) = 130.6$ Hz) [30]. The square planar geometry around rhodium was maintained for all three systems. The PH_3 molecule has P–H bonds of 1.4 Å and H–P–H angles of 109.5. All computations were performed using the QCPE 474 program [32] implemented on an ICIM-6000 computer.

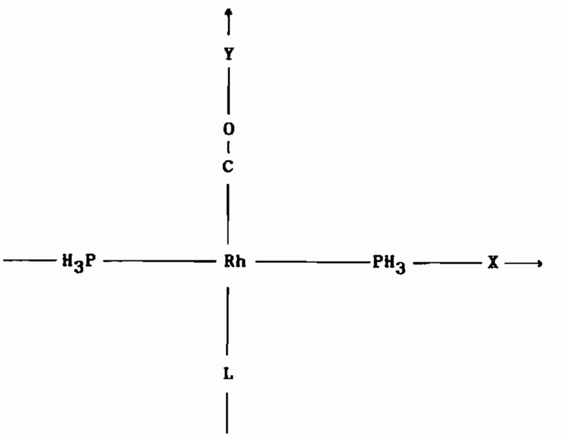

Fig. 1. Coordinate system for *trans*-$[Rh(CO)L(PH_3)_2]$ (L = NSO, SH, Cl); *Z* axis is out of plane.

(a) Preparation of trans-carbonyl(sulfonylnitride)bis(triphenylphosphine)rhodium(I), $[Rh(CO)(NSO)_2)(PPh_3)_2]$

A solution of $CsNSO_2$ (0.21 g, 1 mmol) in acetonitrile (75 ml) was added to a solution of $[Rh(CO)F(PPh_3)_2]$ (0.67 g, 1 mmol) in acetonitrile (25 ml). The reaction mixture was refluxed for 4 h

TABLE 2. Important IR frequencies (cm^{-1}) of the complexes

Complex	ν(CO)	ν(NS)	Bands due to –NSO and –NSO$_2$ ligands	Bands due to S$_3$N ligand
[Rh(CO)(NSO$_2$)(PPh$_3$)$_2$]	1982		1230, 950	
[Ir(CO)(NSO$_2$)(PPh$_3$)$_2$]	1970		1225, 950	
[Ru(CO)(NSO$_2$)$_2$(PPh$_3$)$_2$]	1945		1205, 970	
Cs$_2$[Ru(NS)(NSO$_2$)$_2$Cl$_3$]		1320	1225, 980	
Cs$_2$[Os(NS)(NSO$_2$)$_2$Cl$_3$]		1305	1225, 970	
[Rh(CO)(NSO)(PPh$_3$)$_2$]	1985		1240, 1040, 580	
[Ir(CO)(NSO)(PPh$_3$)$_2$]	1975		1245, 1060, 565	
[Rh(S$_3$N)(PPh$_3$)$_2$]				1020, 615
[Rh(CO)(S$_3$N)(PPh$_3$)]	2070			970, 620

TABLE 3. Parameters used in CNDO/2 calculations

Atom		Orbital exponent	Beta	Mulliken's electronegativity	Subshell Mulliken's electronegativity
Rh	5s	1.360	−19.357	2.28	6.1074
	5p	1.360	−19.357	2.28	1.4463
	4d	2.775	−21.127	2.28	7.7590
Cl	3s	2.033	−22.330	3.16	21.5910
	3p	2.033	−22.330	3.16	8.7080
S	3s	1.817	−18.150	2.58	17.6500
	3p	1.817	−18.150	2.58	6.6890
P	3s	1.600	−15.070	2.19	14.0330
	3p	1.600	−15.070	2.19	5.4640
O	2s	2.275	−31.000	3.44	25.3902
	2p	2.275	−31.000	3.44	9.1110
N	2s	1.950	−25.000	3.04	19.3160
	2p	1.950	−25.000	3.04	7.2750
C	2s	1.625	−21.000	2.55	14.0510
	2p	1.625	−21.000	2.55	5.5720
H	1s	1.200	−09.000	2.20	7.1761

and filtered. The solution was concentrated to 15 ml under reduced pressure. On cooling, yellow crystals of [Rh(CO)(NSO$_2$)(PPh$_3$)$_2$] separated; they were filtered, washed twice with cold acetonitrile (5 ml) and dried under nitrogen atmosphere (yield 0.57 g, 85%). Molecular weight (field desorption MS): (obs.), 733.5 (calc.).

(b) Preparation of trans-carbonyl(sulfonylnitride)bis-(triphenylphosphine)iridium(I), [Ir(CO)(NSO$_2$)(PPh$_3$)$_2$]

A solution of CsNSO$_2$ (0.21 g, 1 mmol) in acetonitrile (75 ml) was added to a solution of Ir(CO)F(PPh$_3$)$_2$ (0.76 g, 1 mmol) in acetonitrile (30 ml). The reaction mixture was refluxed for 4 h and the yellow crystalline complex [Ir(CO)(NSO$_2$)-(PPh$_3$)$_2$] was isolated by a procedure similar to that given in (a) (yield 0.63 g, 77%). Molecular weight: 822 (obs.), 822.8 (calc.).

(c) Preparation of trans-carbonyl(thionitro)bis-(triphenylphosphine)rhodium(I), [Rh(CO)(NSO)(PPh$_3$)$_2$]

Triphenylphosphine (0.1 g) was added to a hot solution of [Rh(CO)(NSO)$_2$)(PPh$_3$)$_2$] (0.2 g) in acetonitrile (20 ml). The resulting solution was refluxed for 2 h and the solution was concentrated to 10 ml under reduced pressure. On cooling, yellow crystals of [Rh(CO)(NSO)(PPh$_3$)$_2$] separated; they were filtered, washed with cold acetonitrile (3 ml) and dried under nitrogen atmosphere (yield 0.13 g, 67%). Molecular weight: 717 (obs.), 717.5 (calc.).

(d) Preparation of trans-carbonyl(thionitro)bis-(triphenylphosphine)iridium(I), [Ir(CO)(NSO)(PPh$_3$)$_2$]

Method A

A solution of CsNSO$_2$ (0.21 g, 1 mmol) in acetonitrile (75 ml) was added to a solution of

$[IrH(CO)(PPh_3)_3]$ (1.0 g, 1 mmol) in acetonitrile (50 ml). The reaction mixture was refluxed for 5 h. The yellow crystalline complex $[Ir(CO)(NSO)(PPh_3)_2]$ was isolated by a procedure similar to that given in (a) (yield 0.44 g, 55%). Molecular weight: 806 (obs.), 806.8 (calc.)

Method B

Triphenylphosphine (0.1 g) was added to a hot solution of $[Ir(CO)(NSO_2)(PPh_3)_2]$ (0.2 g) in acetonitrile (20 ml). The yellow solution was refluxed for 2 h and yellow crystals of $[Ir(CO)(NSO)(PPh_3)_2]$ were isolated by a procedure similar to that given in (c) (yield 0.10 g, 52%).

(e) Preparation of carbonyldi(sulfonylnitride)bis(triphenylphosphine)ruthenium(II), $[Ru(CO)(NSO)_2]_2(PPh_3)_2]$

A solution of $CsNSO_2$ (0.64 g, 3 mmol) in acetonitrile (200 ml) was added to a solution of $[RuH_2(PPh_3)_3]$ (0.91 g, 1 mmol) in dichloromethane (50 ml) under nitrogen atmosphere. The reaction mixture was refluxed for 36 h and then filtered under nitrogen atmosphere. The filtrate was concentrated under vacuum to 25 ml. On cooling the filtrate, light pink crystals of $[Ru(CO)(NSO_2)_2(PPh_3)_2]$ separated; they were filtered under nitrogen atmosphere, washed twice with acetonitrile and under nitrogen atmosphere (yield 0.39 g, 54%).

(f) Preparation of cesium trichlorodi(sulfonylnitride)thionitrosylruthenium(II), $Cs_2[Ru(NS)(NSO_2)_2Cl_3]$

A solution of $CsNSO_2$ (0.42 g, 2 mmol) in acetonitrile (150 ml) was added to a solution of $[Ru(NS)Cl_3]$ (0.25 g, 1 mmol) in acetonitrile (20 ml) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 10 h and filtered under nitrogen atmosphere. The filtrate was concentrated to dryness. The brown residue was washed with cold acetonitrile and dried under vacuum.

(g) Preparation of cesium trichlorodi(sulfonylnitride)thionitrosylosmium(II), $Cs_2[Os(NS)(NSO_2)_2Cl_3]$

The orange crystals of $Cs_2[Os(NS)(NSO_2)_2Cl_3]$ were prepared by a procedure similar to that given in (f) using $CsNSO_2$ (0.42 g, 2 mmol) in acetonitrile (150 ml) and $[Os(NS)Cl_3]$ (0.34 g, 1 mmol).

(h) Preparation of disulfidothionitratobis(triphenylphosphine)rhodium(I), $[Rh(S_3N)(PPh_3)_2$

A solution of S_7NH (0.25 g, 1 mmol) in methanol (30 ml) and of KOH (0.13 g) in methanol (10 ml) were added successively to a suspension of $[RhCl(PPh_3)_3]$ (0.92 g, 1 mmol) in 50 ml methanol under nitrogen atmosphere. The reaction mixture was stirred for 24 h. The light brown solid, thus obtained, was filtered, washed with methanol and dried in vacuum. The crude product was dissolved in dichloromethane (60 ml) and filtered under nitrogen atmosphere. The filtrate was reduced to 15 ml under reduced pressure. On addition of n-hexane (50 ml), a light brown complex $[Rh(S_3N)(PPh_3)_2]$ precipitated out; it was filtered, washed with n-hexane and dried in vacuum (yield 0.42 g, 58%).

(i) Preparation of carbonyldisulfidothionitrato(triphenylphosphine)rhodium(I), $[Rh(CO)(S_3N)(PPh_3)]$

The reddish yellow complex $[Rh(CO)(S_3N)(PPh_3)]$ was prepared by a procedure similar to (h) using S_7NH (0.25 g) in methanol (30 ml) KOH (0.13 g) in methanol (10 ml) and $[Rh(CO)Cl(PPh_3)_2]$ (0.69 g, 1 mmol) in methanol (50 ml) (yield 0.19 g, 41%).

Results and discussion

The reactions of equimolar quantities of $CsNSO_2$ and fluoro complexes $[M(CO)F(PPh_3)_2]$ in acetonitrile under nitrogen atmosphere afford sulfonylnitrido complexes:

$$[M(CO)F(PPh_3)_2] + CsNSO_2 \longrightarrow [M(CO)(NSO_2)(PPh_3)_2] + CsF$$

1, M = Rh; **2**, M = Ir

Complexes **1** and **2** are yellow, air sensitive solids. The IR spectrum of **1** exhibits absorption bands ν(CO), 1982; ν(SO), 1230; ν(NS), 950 cm^{-1} besides the bands of triphenylphosphine. The mass spectrum of **1** shows the decomposition of the complex, and the relative abundances of the fragments $Rh-CO^+$ (*m/e*, 131) and $Rh-NSO_2{}^+$ (*m/e*, 181) are 1.7 and 0.8, respectively. Molecular weight, obtained by field desorption mass spectrometry, is 733. Complex **2** shows IR absorption bands ν(CO), 1970; ν(SO), 1225; ν(NS), 950 cm^{-1} besides the bands due to triphenylphosphine; molecular weight 822.

Complexes **1** and **2** oxidize triphenylphosphine to triphenylphosphineoxide and give thionitro complexes, *trans*-$[M(CO)(NSO)(PPh_3)_2]$ which are also prepared by the reaction of $CsNSO_2$ with hydrido complexes $[MH(CO)(PPh_3)_2$.

$$[M(CO)(NSO_2)(PPh_3)_2] + PPh_3 \longrightarrow [M(CO)(NSO)(PPh_3)_2 + OPPh_3$$

$$[MH(CO)(PPh_3)_3] + CsNSO_2 \longrightarrow [M(CO)(NSO)(PPh_3)_2] + OPPh_3 + \ldots$$

3, M = Rh [4]; **4**, M = Ir

Complexes **3** and **4** are yellow, air sensitive solids. Complex **3** shows IR absorption bands ν(CO), 1985; ν_{as}(NSO), 1240; ν_s(NSO), 1050; δ(NSO), 580 cm^{-1}; molecular weight 717. Complex **4** shows IR absorption bands ν(CO), 1975; ν_{as}(NSO), 1245; ν_s(NSO), 1060; δ(NSO), 565 cm^{-1}; molecular weight 806.

The low value of ν(CO) in these complexes suggests the oxidation of metal is +1. The formation of complexes **3** and **4** from **1** and **2** by the reaction of triphenylphosphine suggest that in **1** and **2**, the CO and NSO_2 groups are *trans* to each other and the NSO_2 ligand is bonded through the nitrogen atom.

$CsNSO_2$ reacts with $[RuH_2(CO)(PPh_3)_2]$ to give $[Ru(CO)(NSO_2)_2(PPh_3)_2]$ (**5**). Complex **5** is a light pink solid. It shows absorption bands at 1945 cm^{-1} due to ν(CO), 1225 cm^{-1} due to ν(SO) and 970 cm^{-1} due to ν(NS) besides the bands of triphenylphosphine. The reactions of $CsNSO_2$ with $[M'(NS)Cl_3]$ in acetonitrile yield thionitrosyl–sulfonylnitrido complexes:

$$[M'(NS)Cl_3] + 2CsNSO_2 \longrightarrow Cs_2[M'(NS)(NSO_2)_2Cl_3]$$

6, M' = Ru; **7**, M' = Os

The IR spectrum of complex **6** exhibits absorption bands at 1320 cm^{-1} due to the NS stretching frequency of the thionitrosyl group [9, 10, 33] and at 1225 and 980 cm^{-1} due to the coordinated NSO_2 group. Complex **7** shows absorption bands ν(NS) at 1305 cm^{-1}, and at 1225 and 970 cm^{-1} due to the coordinated NSO_2 group.

Reactions of heptasulfurimide with rhodium complexes $[RhCl(PPh_3)_3]$ and $[Rh(CO)Cl(PPh_3)_2]$ afford disulfidothionitrato complexes $[Rh(S_3N)(PPh_3)_2]$ (**8**) and $[Rh(CO)(S_3N)(PPh_3)]$ (**9**), respectively. Deprotonation of S_7NH with a base produces the S_4N^- anion.

$$S_7NH \xrightarrow{\text{base}} S_4N^- + \tfrac{3}{8}S_8 + H^+$$

The S_4N^- anion reacts with triphenylphosphine to give the S_3N^- anion and $SPPh_3$ [34].

$$S_4N^- + PPh_3 \longrightarrow S_3N^- + SPPh_3$$

The reactions of S_7NH with $[RhCl(PPh_3)_3]$ and $[Rh(CO)(Cl)(PPh_3)_2]$ are represented as

$$[RhCl(PPh_3)_3] + S_7NH \longrightarrow [Rh(S_3N)(PPh_3)_2] + \tfrac{3}{8}S_8 + SPPh_3 + H^+ + Cl^-$$

$$[Rh(CO)Cl(PPh_3)_2] + S_7NH \longrightarrow [Rh(CO)(S_3N)(PPh_3)] + \tfrac{3}{8}S_8 + SPPh_3 + H^+ + Cl^-$$

The IR spectrum of $[Rh(S_3N)(PPh_3)_2]$ shows bands at 1020 and 615 cm^{-1} assigned to the bidentate S_3N ligand. Complex $[Rh(CO)(S_3N)(PPh_3)]$ shows IR absorption bands at 2070 cm^{-1} due to ν(CO), and at 970 and 620 cm^{-1} due to the S_3N ligand. In the IR spectra of these complexes, the bands around 740 cm^{-1} due to the S_3N ligand mask the bands of triphenylphosphine.

Electronic structure and bonding in trans-[Rh(CO)L(PH$_3$)$_2$] (L = NSO, SH, Cl)

Wiberg indices

A comparison of the C–O, Rh–C and Rh–L Wiberg indices [35] is shown in Fig. 2 and the results are summarized in Table 4. The CO ligand acts as a σ-donor by donating electrons to rhodium and also as a π-acceptor by accepting electrons from rhodium. σ-donation tends to raise $W_{C\text{–}O}$ since electrons are removed from the antibonding σ-orbital while π-backbonding tends to decrease $W_{C\text{–}O}$ because the electrons enter into the antibonding π^* orbital. The increasing values of CO Wiberg indices from [RhSH] < [RhNSO] < [RhCl] suggest that the Rh–C π-backbonding becomes less for the [RhCl] complex and more for the [RhSH] complex. The values of the Rh–C Wiberg indices, which are a reverse of the trend of the C–O Wiberg indices, confirm the above statement. The trend in the Rh–L Wiberg indices is [RhSH] > [RhCl] > [RhNSO]. The largest difference between the components of the Rh–L bonds occurs with Rh(p)–L components. The Rh(s)–L and Rh(p)–L fractional bond indices are both larger for the [RhSH] and [RhCl] complexes while the Rh(d)–L fractional bond index is larger for the [RhNSO] complex. But the sum of the

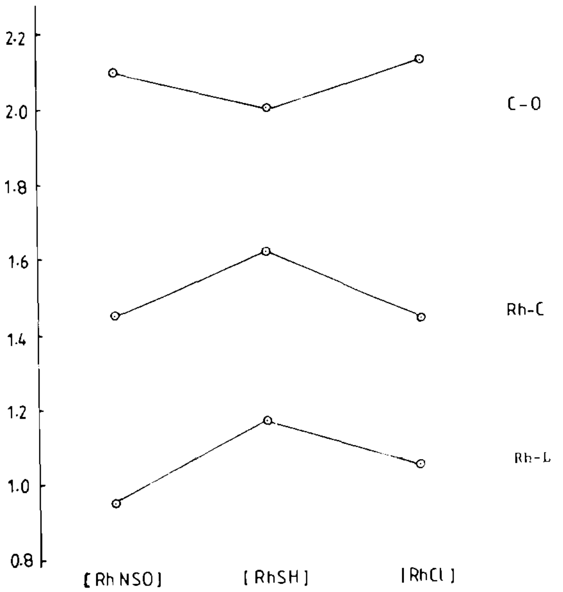

Fig. 2. C–O, Rh–C and Rh–L Wiberg indices for *trans*-$[Rh(CO)L(PH_3)_2]$.

TABLE 4. C–O, Rh–C and Rh–L bond strengths (Wiberg indices) for [Rh(CO)L(PH$_3$)$_2$] (L = NSO, SH, Cl)

	[Rh(CO)(NSO)(PH$_3$)$_2$]	[Rh(CO)(SH)(PH$_3$)$_2$]	[Rh(CO)Cl(PH$_3$)$_2$]
C–O	2.1049	1.9984	2.1267
σ	0.9669	0.9689	0.9670
π	1.1380	1.0295	1.1597
Rh–C	1.4563	1.6158	1.4345
σ	0.7981	0.8447	0.7961
π	0.6582	0.7711	0.6384
Rh(s)–C	0.1875	0.2058	0.1983
Rh(p)–C	0.5486	0.5628	0.5222
Rh(d)–C	0.7202	0.8472	0.7140
Rh–L	0.9532	1.1674	1.0443
σ	0.7404	0.7931	0.7521
π	0.2128	0.3743	0.2922
Rh(s)–L	0.1440	0.1931	0.1795
Rh(p)–L	0.4840	0.7022	0.6380
Rh(d)–L	0.3252	0.2721	0.2268

TABLE 5. Orbital charges and gross atomic charges for *trans*-[Rh(CO)L(PH$_3$)$_2$] (L = NSO, SH, Cl)

System	Orbital charges						Atomic charges
[Rh(CO)(NSO)(PH$_3$)$_2$]							
	Rh		N				
	5s	0.6791	2s	1.4326			Rh = −0.8762
	5p$_x$	0.5749	2p$_x$	1.4607			N = −0.2638
	5p$_y$	0.5750	2p$_y$	1.4551			S = 0.5752
	5p$_z$	0.4180	2p$_z$	0.9151			O(NSO) = −0.5245
	4d$_{z^2}$	1.9046					C = 0.2780
	4d$_{xz}$	1.9453	S				
	4d$_{yz}$	1.4823					
	4d$_{x^2-y^2}$	0.5083	3s	1.6761			O(CO) = −0.2034
	4d$_{xy}$	1.7884	3p$_x$	1.1512			
			3p$_y$	1.4494			
			3p$_z$	1.1481			
	O(NSO)		C		O(CO)		
	2s	1.8085	2s	1.2271	2s	1.6938	
	2p$_x$	1.0449	2p$_x$	0.6719	2p$_x$	1.4955	
	2p$_y$	1.9466	2p$_y$	1.0282	2p$_y$	1.4482	
	2p$_z$	1.7245	2p$_z$	0.7949	2p$_z$	1.5659	
[Rh(CO)(SH)(PH$_3$)$_2$]							
	Rh		S				
	5s	0.6948	3s	1.6729			Rh = −0.9183
	5p$_x$	0.5772	3p$_x$	1.1608			S = −0.1323
	5p$_y$	0.6232	3p$_y$	1.5430			H = 0.0057
	5p$_z$	0.4599	3p$_z$	1.7556			C = 0.2783
	4d$_{z^2}$	1.9374					O = −0.2539
	4d$_{xz}$	1.9519					
	4d$_{yz}$	1.3695					
	4d$_{x^2-y^2}$	0.5175					
	4d$_{xy}$	1.7869					

(*continued*)

TABLE 5 (*continued*)

System	Orbital charges				Atomic charges
	C		O		
	2s	1.2052	2s	1.7059	
	$2p_x$	0.6707	$2p_x$	1.5119	
	$2p_y$	1.0289	$2p_y$	1.4061	
	$2p_z$	0.8169	$2p_z$	1.6300	
$[Rh(CO)Cl(PH_3)_2]$	Rh		Cl		
	5s	0.6879	3s	1.8168	Rh = −0.8537
	$5p_x$	0.5733	$3p_x$	1.9744	Cl = −0.2434
	$5p_y$	0.5943	$3p_y$	1.6264	C = 0.2804
	$5p_z$	0.3960	$3p_z$	1.8258	O = −0.1932
	$4d_{z^2}$	1.9338			
	$4d_{xz}$	1.9505			
	$4d_{yz}$	1.4728			
	$4d_{x^2-y^2}$	0.4283			
	$4d_{xy}$	1.8168			
	C		O		
	2s	1.2350	2s	1.6956	
	$2p_x$	0.6667	$2p_x$	1.4845	
	$2p_y$	1.0282	$2p_y$	1.4461	
	$2p_z$	0.7897	$2p_z$	1.5670	

differences of the Rh(s)–L and Rh(p)–L fractional bond indices for the [RhSH] and [RhCl] complexes as compared to the [RhNSO] complex is greater than the difference of the Rh(d)–L components and hence disfavour the Rh–NSO bond.

In order to see in more detail how the substitution of an L ligand (L = NSO, SH, Cl) affects the bonding patterns, it is necessary to examine the various contributions to the Rh–C, C–O and Rh–L bond orders for $[Rh(CO)L(PH_3)_2]$. The following points are apparent: (i) the main contributions to the Rh–C bond order are from the interactions of Rh($5s_\sigma$, $5p_\sigma$ and $4d_\sigma$) with C($2s_\sigma$ and $2p_\sigma$) and the net σ-electron donation increases in the order SH < NSO < Cl; (ii) the interactions of Rh($5p_\pi$ and $4d_\pi$) to C($2p_\pi$) contribute 8–90% of the σ-electron contribution; (iii) the interactions of Rh($4d_\pi$) to C($2p_\pi$) constitute a strong π-field while the same interactions are very weak for the *trans* Rh–L bond; (iv) for oxygen of the carbonyl group, the more negative charge and larger $2p_\pi$ population for the [RhSH] complex is indicative of greater π-backbonding; (v) the π-acceptor to σ-donor ratio for the CO group decreases in the order [RhSH] > [RhNSO] > [RhCl]. The bonding model consistent with these observations is that if π-backbonding from the metal is the important factor determining metal–ligand bond order, the metal–ligand bond order should be greater for the ligand having more π-acceptor to σ-donor ratio.

Several points are apparent from the various contributions to the Rh–L (L = NSO, SH, Cl) bond order: (i) the main contributions to the Rh–L bond order are from the interactions of Rh($5s_\sigma$, $5p_\sigma$ and $4d_\sigma$) with L(s_σ and p_σ) atomic orbitals; (ii) the interactions of Rh($5p_\pi$ and $4d_\pi$) to L(p_π) contribute 29–47% of the σ-electron contribution; (iii) π-backbonding decreases in the order SH > Cl > NSO, that is, the NSO group is the worst π-acceptor amongst three ligands.

Charge distribution

Orbital charges and gross atomic charges are presented in Table 5. The variation of charge on rhodium, CO and ligand L (L = NSO, SH, Cl) is shown in Fig. 3. The charges on *trans* ligand L are negative and the trend in L charges is [RhCl] > [RhNSO] > [RhSH], which is the reverse of the trend of the Rh charges. These results suggest that Cl is a better electron remover from the central rhodium atom. The Mulliken population analysis assigns positive charges of +0.0746, +0.0244 and +0.0872 on the carbonyl group for $[Rh(CO)L(PH_3)_2]$ (L = NSO, SH, Cl), respectively. The trend in carbonyl charges is the same as the trend of the C–O Wiberg indices

TABLE 6. Frontier orbital of $[Rh(CO)(NSO)(PH_3)_2]$

Orbital	Energy (eV)	Main components of orbital
8a″(LUMO)	+0.1417	$+0.1537(C\ 2p_z)+0.1177(P\ 3p_y)+0.2579(P\ 3p_z)$ $+0.1080(P\ 3p_z)-0.1673(O\ 2p_z)+0.5940(H\ 1s)$ $-0.3515(S\ 3p_z)+0.2653(O\ 2p_z)+0.4206(Rh\ 5p_z)$ $-0.3210(Rh\ 4d_{yx})$
7a″(HOMO)	−7.8940	$-0.2502(C\ 2p_z)+0.3940(O\ 2p_z)-0.1103(S\ 3p_z)$ $+0.1673(O\ 2p_z)-0.2587(Rh\ 5p_z)-0.7733(Rh\ 4d_{yz})$ $+0.1023(Rh\ 4d_{xy})$
18a′	−8.4248	$-0.1244(C\ 2p_x)-0.2303(N\ 2p_x)-0.1040(N\ 2p_y)$ $+0.2276(O\ 2p_x)-0.1244(Rh\ 4d_{xz})-0.1212(Rh\ 4d_{yz})$ $-0.8457(Rh\ 4d_{xy})$
17a′	−9.2311	$+0.2393(N\ 2p_y)-0.2103(S\ 3p_y)+0.1973(O\ 2p_y)$ $+0.8373(Rh\ 4d_{z^2})-0.2068(Rh\ 4d_{x^2-y^2})$ $-0.1487(Rh\ 4d_{xy})$
6a″	−9.2893	$+0.9456(Rh\ 4d_{xz})+0.1342(Rh\ 4d_{xy})$

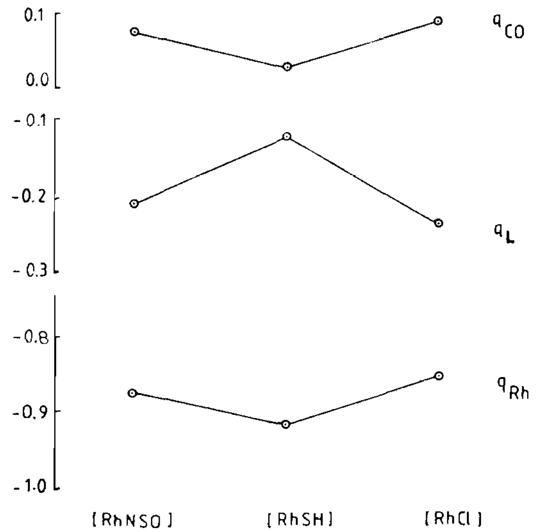

Fig. 3. Charge distributions (q) in *trans*-$[Rh(CO)L(PH_3)_2]$.

and the reverse of the trend of the Rh–C Wiberg indices. Thus, the CO charges are correlated with traditional π-backbonding concepts.

Energy levels in trans-[Rh(CO)(NSO)(PH₃)₂]

In Table 6 the energies and salient features of the frontier orbitals of *trans*-$[Rh(CO)(NSO)(PH_3)_2]$ which consist mostly of rhodium d-orbitals are given. We note that the highest occupied molecular orbital is an orbital of symmetry localized on RhCO. The unoccupied orbital of lowest energy can well be described as π* (H_3P-Rh-PH_3).

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References

1 K.K. Pandey and U. C. Agarwala, *Indian J. Chem.*, *20A* (1981) 906.
2 K. C. Jain, K. K. Pandey and U. C. Agarwala, *Indian J. Chem.*, *20A* (1981) 1022.
3 R. D. Tewari, K. K. Pandey and U. C. Agarwala, *Inorg. Chem.*, *21* (1981) 845.
4 H. W. Roesky, K. K. Pandey, B. Krebs and M. Dartmann, *J. Chem. Soc., Dalton Trans.*, (1984) 2271.
5 M. Herberhold, F. Neumann, G. Suss-Fink and U. Thewalt, *Inorg. Chem.*, *26* (1987) 3612.
6 R. Short, M. B. Hursthouse, T. G. Purcell and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, (1987) 407.
7 H. Plenio, H. W. Roesky, M. Noltemeyer, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, (1987) 1483.
8 I. P. Perkin, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, *8* (1989) 835.
9 P. F. Kelly and J. D. Woollins, *Polyhedron*, *5* (1986) 607.
10 T. Chivers and F. Edelmann, *Polyhedron*, *5* (1986) 1661.
11 R. Jones, T. G. Purcell, D. J. Williams and J. D. Woollins, *Polyhedron*, *6* (1987) 2168.
12 K. K. Pandey and M. Massoudipour, *Inorg. Chim. Acta*, *138* (1987) 169.
13 K. K. Pandey, D. T. Nehete and M. Massoudipour, *Inorg. Chim. Acta*, *129* (1987) 253.
14 R. Jones, T. G. Purcell, D. J. Williams and J. D. Woollins, *Polyhedron*, *7* (1988) 647.
15 H. W. Roesky, W. Schieder, W. Isenberg, D. Bohler and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, *21* (1982) 153.

16 H. G. Heal and J. Kane, *Inorg. Synth., 11* (1968) 184.

17 L. Vaska and J. Poene, *J. Chem. Soc., Chem. Commun.*, (1974) 418.

18 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth., 15* (1974) 59.

19 L. Vaska and S. S. Bath, *J. Am. Chem. Soc., 85* (1963) 3500.

20 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth., 15* (1974) 45.

21 D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth., 11* (1968) 99.

22 J. A. Osborn, F. H. J. Jordine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A,* (1966) 1711.

23 J. W. Bats, K. K. Pandey and H. W. Roesky, *J. Chem. Soc., Dalton Trans.*, (1984) 2081.

24 K. K. Pandey, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Z. Naturforsch., Teil B, 39* (1984) 590.

25 A. I. Vogel, *A Text Book of Quantitative Analysis,* Longmans Green, London, 3rd edn., 1961.

26 A. Baba-Ahmad and J. Gayoso, *Theor. Chim. Acta, 62* (1983) 507.

27 G. Burns, *J. Chem. Phys., 41* (1964) 1521.

28 J. A. Pople and D. Beveridge, *Approximate Molecular Orbital,* McGraw Hill, New York, 1970.

29 R. S. Mulliken, *J. Chem. Phys., 23* (1955) 1833.

30 T. R. Gaffney and J. A. Ibers, *Inorg. Chem., 21* (1982) 2857.

31 A. D. Pra, G. Zanotti and P. Segala, *Cryst. Struct. Commun., 8* (1979) 959.

32 A. Baba-Ahmed, J. Gayoso, B. Maouche and O. Ouamerali, *QCPE,* (1985) 475.

33 H. W. Roesky and K. K. Pandey, *Adv. Inorg. Radiochem., 26* (1983) 337.

34 J. Bojes, T. Chivers, W. G. Laidlaw and M. Trsic, *J. Am. Chem. Soc., 104* (1982) 4837.

35 K. A. Wiberg, *Tetrahedron, 24* (1968) 1083.