DALTON COMMUNICATION

Synthesis and crystal structures of η^2-sulfenamido complexes of ruthenium and nickel, and of chromium imido and cobalt iminophosphorane complexes *via* sulfenamido rearrangement†

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The interaction of $[Ru(\eta\text{-}C_5Me_5)Cl_2]_2$ with $Li(Bu^tNSPh)$, gave two products, $Ru(\eta^4\text{-}C_5Me_4CH_2)(\eta^2\text{-}Bu^tNSPh)Cl$ **1** and the dimer $Cl(\eta\text{-}C_5Me_5)Ru(\mu\text{-}NBu^t)(\mu\text{-}SPh)Ru(\eta\text{-}C_5Me_5)$ **2**; the former is best described as a η^4-tetramethylfulvene ruthenium(II) complex, while in the latter the bridging *tert*-butylimido and benzenethiolato groups were formed by S–N cleavage of sulfenamido species. A similar cleavage resulted in the formation of $Cr^V(\eta\text{-}C_5Me_5)(NBu^t)(SPh)_2$ **3**, in the interaction of $Li(Bu^tNSPh)$ with $[Cr(\eta\text{-}C_5Me_5)Br_2]_2$. Interaction of $CoCl_2(PMe_3)_3$ with $Li(p\text{-}MeC_6H_4NSPh)$ gave the iminophosphorane complex $Co(p\text{-}MeC_6H_4NPMe_3)_2(SPh)_2$ **4**. Interaction of $NiCl_2(PMe_3)_2$ with $Li(Bu^tNSPh)$ gave $Ni(\eta^2\text{-}Bu^tNSPh)_2(PMe_3)$ **5**. The structures of compounds **1**–**5** have been confirmed by X-ray crystallography.

We have recently described a series of η^2-sulfenamido complexes of titanium, zirconium, molybdenum and tungsten.[1] These were obtained by interaction of electrophilic metal halides with $Li(Bu^tNSR)$, R = Ph or mesityl, or by interaction of PhSCl with the electron-rich, homoleptic *tert*-butylimido compound $Li_2W(NBu^t)_4$. The latter method, resulting in nitrogen–sulfur bond formation in the co-ordination sphere of the metal, was extended to the synthesis of selenamido complexes.

This paper describes sulfenamido complexes of ruthenium and nickel prepared by the salt elimination method as before, as well as products obtained by sulfur–nitrogen bond cleavage, leading to *tert*-butylimidothiolato complexes of ruthenium and chromium and iminophosphoranethiolato complexes of cobalt. Analytical and physical data for the new compounds are given in Table 1.

Results and Discussion

Ruthenium complexes

Interaction of $[Ru(\eta\text{-}C_5Me_5)Cl_2]_2$ with 2 equivalents of $Li(Bu^tNSPh)$ in toluene gave low yields of two products **1** and **2** which were separated by fractional crystallisation from light petroleum. No products can be obtained in solvents other than toluene or when the lithium reagent is not freshly prepared. The latter point might be due to inactive polymer formation on ageing, and correlated with the decreasing solubility of the lithium reagent in toluene after long periods (> 2 weeks at −20 °C). Compounds **1** and **2** are moderately air stable and although their thermal robustness allowed observation of the molecular ion in the mass spectrum (electron impact, EI), their structures were unequivocally determined by X-ray crystallography. Diagrams of the molecules are shown in Figs. 1 and 2; selected bond lengths and angles are in Tables 2 and 3, respectively. In **1** the ruthenium centre is bound to one chloride, one η^2-*tert*-butylsulfenamido ligand and a distorted $C_5Me_4CH_2$ fragment.

The electronic structure of the $C_5Me_4CH_2$ ligand is described by the limiting forms **a** and **b**. The first, a neutral tetramethylfulvene ligand, can act as a $6e^-$ (η^4, η^2) donor; whilst the second **b**, a methylenetetramethylcyclopentadienyl dianionic ligand, is formally an $8e^-$ donor. Examples of both descriptions have been given in the literature.[2] Assignment of the structure of **1** as a tetramethylfulvene complex was based on careful consideration and comparison of structural parameters with those already known. Within the co-ordinated $C_5Me_4CH_2$, shown in diagram I, the C(3)–C(8), C(1)–C(2) and C(4)–C(5)

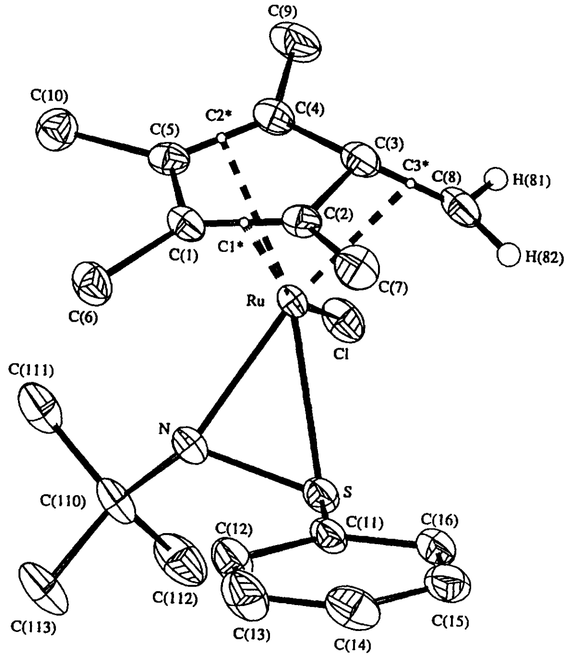
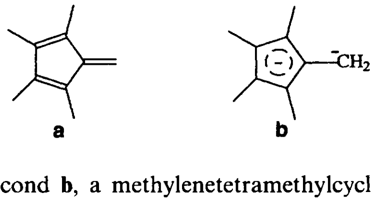


Fig. 1 The structure of $Ru(\eta^4\text{-}C_5Me_4CH_2)(\eta^2\text{-}Bu^tNSPh)Cl$ **1**, 40% probability ellipsoids. The experimentally located hydrogen atoms, H(81) and H(82), are included but the remaining hydrogen atoms have been omitted for clarity



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† *Non-SI unit employed:* G = 10^{-4} T.

Table 1 Analytical and physical data for new compounds

	Compound	Colour	M.p./°C	Analysis (%)[a] C	H	N
1	$Ru(\eta^6\text{-}C_5Me_4CH_2)(\eta^2\text{-}Bu^tNSPh)Cl$[b]	Orange	198 (decomp.)			
2	$Cl(\eta\text{-}C_5Me_5)Ru(\mu\text{-}NBu^t)(\mu\text{-}SPh)Ru(\eta\text{-}C_5Me_5)$[b]	Brown	195 (decomp.)			
3	$Cr(\eta\text{-}C_5Me_5)(NBu^t)(SPh)_2$	Purple	133–136	64.7 (65.5)	6.9 (7.2)	2.9 (2.9)
4	$Co(p\text{-}MeC_6H_4NPMe_3)_2(SPh)_2$	Green	160–162	59.6 (60.1)	6.5 (6.6)	4.2 (4.4)
5	$Ni(\eta^2\text{-}Bu^tNSPh)_2(PMe_3)$	Blue	98 (decomp.)	55.7 (55.8)	7.2 (7.5)	5.7 (5.7)

[a] Calculated values in parentheses. Mass spectral data are given in the Experimental section. [b] Combustion analysis gave unsatisfactory results.

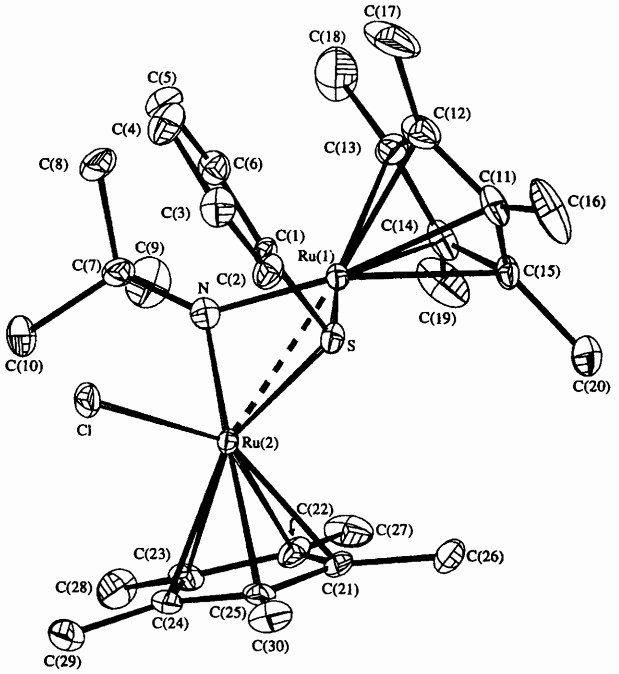
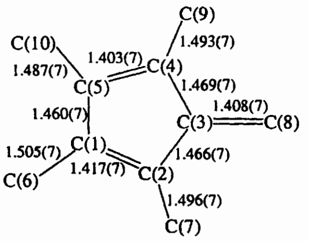


Fig. 2 The structure of $Cl(\eta\text{-}C_5Me_5)Ru(\mu\text{-}Bu^t)(\mu\text{-}SPh)Ru(\eta\text{-}C_5Me_5)$ **2**, 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity



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bond lengths (Å) are much shorter than the other C–C distances, clearly indicating substantial double bond character. This bonding type, observed in the complex $[Ru(C_5Me_4CH_2)Cl(\mu\text{-}Cl)]_2$,[2a,b] may be favoured because of the six ruthenium d electrons available for π back bonding to the olefin. Hence the oxidation state of the ruthenium is II and the electron count of 18 explains the stability of **1**.

The midpoints of the three double bonds (Cl*, C2*, C3*), see Fig. 1, are all equidistant, within experimental error, from the metal centre. The co-ordination geometry can best be described as distorted octahedral, the most common found for Ru^{II}.[3] Two *trans* 'axial' sites of the octahedron are occupied by C2* and sulfur, the C2*–Ru–S bond angle being distorted from the ideal 180° to 162.2(2)°. The 'equatorial' plane is then defined by the atoms Ru, N, Cl, Cl* and C3*. The axial sites S and C2* are equidistant (1.7 Å) above and below this plane.

The Ru–C (C_5 ring) distances fall into three groups; the shortest distance is to C(3) [2.070(3) Å], the next shortest to C(2) and C(4) at 2.181(5) Å and the longest to C(1), C(5) [2.236(5) and 2.246(5) Å]. This feature is clearly a consequence of the co-ordination of the exocyclic double bond between C(3) and C(8). The C_5 ring is planar to within 0.03 Å. Three of the methyl groups are bent out of the plane of the ring, away from the metal centre, as is commonly observed in C_5Me_5M complexes,[4] whereas C(6) is bent 0.059(3) Å towards the Ru. The methylenic carbon, C(8), is bent towards the Ru and is 0.949(3) Å from the C_5 plane, as observed in the complex $[Ru(C_5Me_4CH_2)Cl(\mu\text{-}Cl)]_2$.[2a]

The comparatively short Ru–S distance, only 0.056 Å longer than the sum of the covalent radii, indicates the presence of a strong bond and the sulfenamido ligand appears to be co-ordinating in a truly bidentate fashion. The Ru–Cl bond is *ca.* 0.2 Å longer than the sum of the covalent radii. The N–S bond length [1.672(4) Å] is similar to those observed in previous structures (*ca.* 1.68 Å).[1]

The C–N–S–C torsion angle (59.1°) is small compared with those previously observed (71.9–89.5°).[1] The sulfur is pyramidal [angle sum 277.5(2)°] as is the nitrogen [angle sum 329.3(3)°]. This may be attributed to the correspondingly weaker Ru–N interaction observed, *ca.* 0.17 Å longer than the covalent radii sum, and the absence of N p ——→ Ru d π bonding.

Supporting evidence for the proposed structural assignment was provided by NMR spectroscopy. Thus the ^1H NMR spectrum of compound **1** does not show any hydride resonances in the high field region, while there are two singlets in the region δ 4.5–5.0 assignable to the two methylene protons; no coupling between them is observed. Four singlets (1 : 1 : 1 : 1 ratio) assignable to four inequivalent methyls of the tetramethylfulvene ring are at δ 1.75, 1.65, 1.00 and −0.28. The relatively wide spread of the chemical shifts can be accounted for by the very different chemical environments of the methyl groups caused by the π-electron density (ring current anisotropy) of the aromatic benzenethiolate and *tert*-butylamido groups. The *tert*-butylamido and aromatic protons occur at the expected positions.

The compound **1** can potentially exist as conformers with the idealised geometries shown below. In addition, sulfur invertomers are possible with '*endo*' and '*exo*' phenyl orientation. In all these isomers, assuming a static picture and in the absence of accidental coincidence, the two methylene

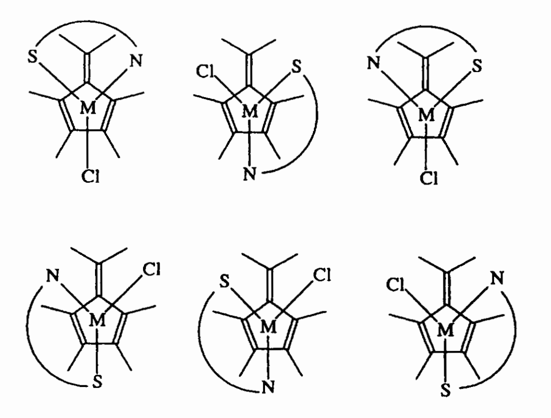


Table 2 Selected bond lengths (Å) and angles (°) for Ru(η^6-$C_5Me_4CH_2$)(η^2-Bu^tNSPh)Cl **1** with estimated standard deviations in parentheses

Ru–N	2.110(4)	Ru–C1*	2.09(1)
Ru–S	2.336(2)	Ru–C2*	2.10(1)
Ru–Cl	2.426(2)	Ru–C3*	2.08(1)
S–N	1.672(4)	S–C(11)	1.775(5)
		N–C(110)	1.505(6)
C1*–Ru–C2*	54.3(2)	C3*–Ru–N	161.4(2)
C1*–Ru–C3*	68.0(2)	S–Ru–Cl	86.9(5)
C1*–Ru–Cl	158.9(1)	N–Ru–Cl	92.0(1)
C1*–Ru–S	114.2(2)	N–Ru–S	43.8(1)
C1*–Ru–N	103.4(2)	N–S–C(11)	106.4(2)
C2*–Ru–C3*	68.1(2)	N–S–Ru	60.9(2)
C2*–Ru–Cl	105.3(2)	C(11)–S–Ru	110.2(2)
C2*–Ru–S	162.2(2)	S–N–Ru	75.3(2)
C2*–Ru–N	121.4(2)	C(110)–N–Ru	135.9(3)
C3*–Ru–Cl	101.0(2)	C(110)–N–S	118.6(3)
C3*–Ru–S	123.0(2)		

C1*, C2* and C3* are the midpoints of the C(1)–C(2), C(4)–C(5) and C(3)–C(8) bonds.

Table 3 Selected bond lengths (Å) and angles (°) for (η^5-C_5Me_5)Ru(μ-NBu^t)(μ-SPh)Ru(η^5-C_5Me_5)Cl **2** with e.s.d.s in parentheses

Ru(1) ··· Ru(2)	2.727(1)	Ru(2)–Cp2*	2.03(6)
Ru(1)–Cp1*	1.94(5)	Ru(2)–Cl	2.410(2)
Ru(1)–N	1.837(6)	Ru(2)–N	2.045(6)
Ru(1)–S	2.283(2)	Ru(2)–S	2.348(2)
N–C(7)	1.470(9)	S–C(1)	1.795(8)
Cp1*–Ru(1)–N	144(2)	Cp2*–Ru(2)–Cl	115(2)
Cp1*–Ru(1)–S	122(2)	Cp2*–Ru(2)–N	135(2)
S–Ru(1)–N	92.3(2)	Cp2*–Ru(2)–S	127.9(14)
Ru(1)–N–C(7)	136.8(4)	Cl–Ru(2)–N	92.0(2)
Ru(2)–N–C(7)	134.1(4)	Cl–Ru(2)–S	88.82(7)
Ru(1)–S–C(1)	110.7(2)	S–Ru(2)–N	85.4(2)
Ru(2)–S–C(1)	114.4(2)	Ru(1)–N–Ru(2)	89.1(2)
		Ru(1)–S–Ru(2)	72.15(6)

Cp1* and Cp2* are the centroids of the pentamethylcyclopentadienyl rings C(11)–C(15) and C(21)–C(25), respectively.

protons are diastereotopic while the four methyl groups are inequivalent. The spectroscopic data given above strongly support the presence of only one isomer in solution. This behaviour is contrasted with Maitlis' observations on the chloro-substituted derivative [Ru($C_5Me_4CH_2$)Cl(μ-Cl)]$_2$.[2a] The spectrum remains unchanged in [$^2H_8$]toluene up to +100 °C. Ruthenium amido complexes are not common.[5]

In the structure of compound **2** the unsymmetrically substituted ruthenium centres Ru(1) and Ru(2) formally both exist in oxidation state III. Atom Ru(1) is bound to a bridging *tert*-butylimide ligand, a bridging phenylthiolate ligand and a pentamethylcyclopentadienyl ligand co-ordinated in an η^5 fashion; Ru(2) is also coordinated to the imide and thiolate ligands, and a C_5Me_5 group, and is additionally bound to a terminal chloride atom. The core atoms Ru(1), Ru(2), N and S are not planar, and a fold angle between Ru(1), N, Ru(2) and Ru(1), S, Ru(2) of 47.0(2)° is observed.

The Ru–C (C_5Me_5) bonds vary from 2.204(7) to 2.329(7) Å for Ru(1), the range of 0.125 Å indicating some slippage or tilting of the ring. For Ru(2) these bond lengths vary from 2.178(7) to 2.266(6) Å and the range (0.088 Å) indicates slightly less distortion than for Ru(1).

In contrast, however, the *tert*-butylimide ligand forms an unsymmetrical bridge, in which the Ru(1)–N bond [1.837(6) Å] is 0.208(6) Å shorter than the Ru(2)–N bond [2.045(6) Å]. The Ru–S bond lengths are similar, differing only by 0.065(2) Å, but the distance to Ru(1), 2.283(2) Å, is again shorter than that to Ru(2), 2.348(2) Å. The N–Ru–S angles differ by *ca.* 7° for the two ruthenium centres [92.3(2) for Ru(1) and 85.4(2)° for Ru(2)]. These variations must be attributed to the different co-ordination numbers.

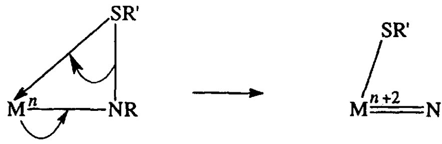
The nitrogen atom is accurately planar (angle sum 360°), whereas the sulfur is pyramidal [angle sum 297.3(2)°]. The difference in geometry of the nitrogen and sulfur atoms is reflected in the bridging Ru(1)–N–Ru(2) and Ru(1)–S–Ru(2) angles, which differ by *ca.* 17° and are 89.1(2) and 72.15(6)°, respectively.

The diamagnetism of compound **2** at room temperature can be accounted for by direct metal–metal interaction [Ru(1) ··· Ru(2) 2.727(1) Å] or superexchange *via* the bridge. The ^1H NMR spectrum of **2** shows the presence of two inequivalent pentamethylcyclopentadienyl rings and *tert*-butylimido protons in the region associated with bridging imido groups. Some bridging or terminal arylimido complexes of ruthenium have been structurally characterised[6] while others were identified spectroscopically[5e,7a] or proposed as intermediates.[7b] To our knowledge, **2** is the first example of a structurally characterised alkylimidoruthenium species.

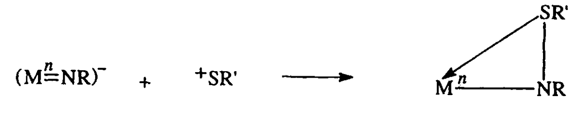
The mechanism of formation of compounds **1** and **2** is not clear. The recently reported isolation of (tetramethylfulvene)-ruthenium(II) complexes by Maitlis and co-workers[2a,b] and the experimental evidence presented for the involvement of [Ru(η-C_5Me_5)Cl_2]$_2$O,[8] formed by oxygenation of [Ru(η-C_5Me_5)Cl_2]$_2$ with molecular oxygen, followed by dehydration to the tetramethylfulvene species prompted us to examine whether involvement of any of these two complexes could explain the formation of **1**. However, independent syntheses according to literature procedures followed by interaction with Li(Bu^tNSPh) in toluene failed to give any detectable amounts of **1** or **2**. Alternatively, initial formation of Ru(η-C_5Me_5)Cl(Bu^tNSPh) from the labile [Ru(η-C_5Me_5)Cl_2]$_2$ and Li(Bu^tNSPh) followed by inter- or intra-molecular reactions could lead to **1**. The formation of **2** could possibly be occurring by a parallel pathway, where, in a monosubstituted dimeric ruthenium complex, the sulfenamido group undergoes sulfur–nitrogen bond cleavage, leading to the observed products (see also below).

The nitrogen–sulfur bond in sulfenamides has been reported to undergo homolytic fission;[9] when co-ordinated to a metal there could be cleavage, as in Scheme 1. This is formally an oxidative addition of the N–S bond to the metal. In contrast, sulfenamido formation in the co-ordination sphere of an imido complex by electrophilic attack, Scheme 2, does not involve change in the oxidation state of the metal. During the formation of **2** nitrogen–sulfur bond cleavage is preceded or followed by reducing processes. Although the involvement of competing reactions in the present ruthenium system makes nitrogen–sulfur bond cleavage of sulfenamido complexes of limited synthetic utility for the preparation of otherwise inaccessible imido species, in principle it constitutes a new method for their preparations. Selenamido complexes are expected to react similarly. Cleavage of S–S bonds by transition-metal complexes has attracted recent attention.[10]

Interaction of other ruthenium complexes, *e.g* Ru(η-C_5Me_5)(OMe) and Ru(η-C_5H_5)(O_2CMe)(PPh_3), gave products which could not be isolated as crystals.



Scheme 1



Scheme 2

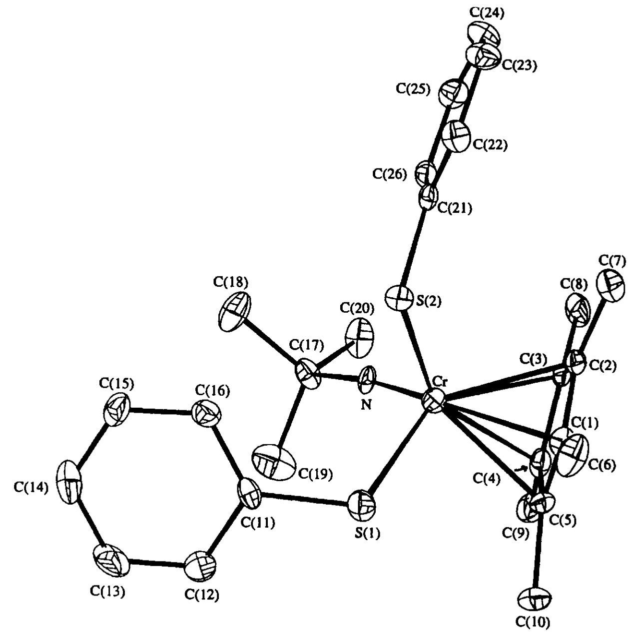


Fig. 3 The structure of $Cr^V(\eta-C_5Me_5)(NBu^t)(SPh)_2$ **3**, 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity

Table 4 Selected bond lengths (Å) and angles (°) for $Cr(\eta^5-C_5Me_5)(NBu^t)(SPh)_2$ **3** with e.s.d.s in parentheses

Cr–Cp*	1.95(2)	N–C(17)	1.470(5)
Cr–N	1.620(3)	S(1)–C(11)	1.760(5)
Cr–S(1)	2.301(2)	S(2)–C(21)	1.744(4)
Cr–S(2)	2.327(2)		
Cp*–Cr–N	128.4(6)	Cr–N–C(17)	172.2(3)
Cp*–Cr–S(1)	111.1(6)	Cr–S(1)–C(11)	111.6(2)
Cp*–Cr–S(2)	114.8(6)	Cr–S(2)–C(21)	108.7(2)
N–Cr–S(1)	101.7(1)	S(1)–Cr–S(2)	90.52(6)
N–Cr–S(2)	103.4(1)		

Cp* is the centroid of the pentamethylcyclopentadienyl ring C(1)–C(5).

Table 5 Selected bond lengths (Å) and angles (°) for $Co(p-MeC_6H_4NPMe_3)_2(SPh)_2$ **4** with e.s.d.s in parentheses

Co–N(1)	2.034(4)	N(1)–C(10)	1.456(6)
Co–N(2)	2.029(3)	N(2)–C(20)	1.427(6)
Co–S(1)	2.290(2)	S(1)–C(31)	1.764(5)
Co–S(2)	2.326(2)	S(2)–C(41)	1.781(5)
P(1)–N(1)	1.600(4)	P(2)–N(2)	1.601(4)
N(1)–Co–N(2)	109.1(1)	C(41)–S(2)–Co	105.2(2)
N(1)–Co–S(1)	113.7(1)	C(10)–N(1)–Co	116.1(3)
N(1)–Co–S(2)	113.1(1)	Co–N(1)–P(1)	128.7(2)
N(2)–Co–S(1)	113.0(1)	P(1)–N(1)–C(10)	114.7(3)
N(2)–Co–S(2)	105.4(1)	C(20)–N(2)–Co	116.0(3)
S(1)–Co–S(2)	102.1(1)	Co–N(2)–P(2)	126.4(2)
C(31)–S(1)–Co	110.1(2)	P(2)–N(2)–C(20)	117.6(3)

Chromium complexes

Interaction of $[Cr(\eta-C_5Me_5)Br_2]_2$ with 2 equivalents of $Li(Bu^tNSPh)$ in toluene did not give the expected chromium(III) sulfenamido species but gave the *tert*-butylimidochromium(v) complex $Cr(\eta-C_5Me_5)(NBu^t)(SPh)_2$ **3**, in moderate yields; the *tert*-butylimido group may be formed after a nitrogen–sulfur bond cleavage of an intermediate sulfenamido complex. The fate of the second Bu^tN group is unknown. Chromium(v) imido complexes, *e.g.* $Cr(NBu^t)Cl_3$, have been described.[11] The structure of **3** is shown in Fig. 3; selected bond lengths and angles are in Table 4.

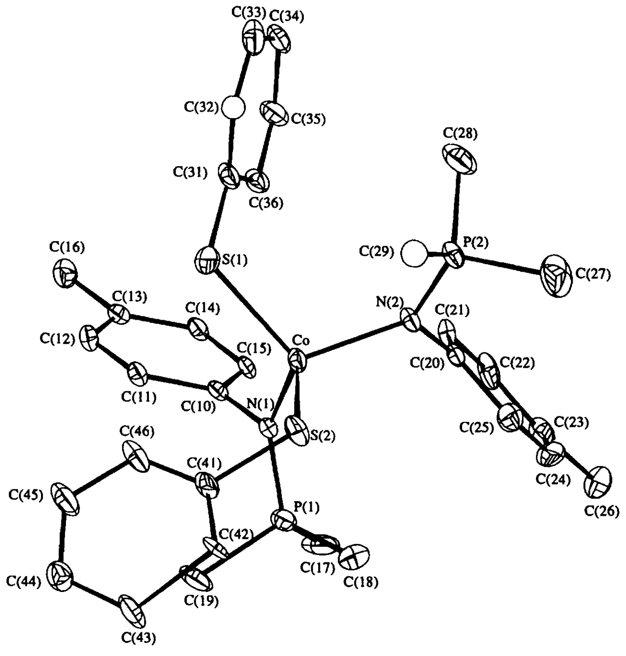


Fig. 4 The structure of $Co(p-MeC_6H_4NPMe_3)_2(SPh)_2$ **4**, 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity

For this complex it is convenient to consider the C_5Me_5 ligand as occupying one co-ordination site, so the Cr atom is tetrahedrally co-ordinated. This geometry is completed by co-ordination of two benzenethiolates and one *tert*-butylimide. The angles within the co-ordination sphere range widely from 90.52(6) to 128.4(6)°, mainly due to the steric requirements of the C_5Me_5 ring. The Cr–C (C_5Me_5) distances range only from 2.244(5) to 2.286(5) Å, and therefore the ring is symmetrically co-ordinated in an η^5 fashion. The ring is planar to within 0.010(5) Å. The plane of the phenyl ring is almost parallel to that of the C_5Me_5 ring at an angle of 7.7(5)°. The *tert*-butylimide ligand is almost linear [Cr–N–C(17) 172.2(3)°] while the Cr–N bond is short [1.620(3) Å]. The Cr–S–C angles at atoms S(1) and S(2) are 111.6(2) and 108.7(2)°, respectively.

Compound **3** is a paramagnetic d^1 species. The ESR spectrum in toluene is temperature dependent; at 77 K it shows a symmetrical signal centred at $g = 1.994$ ($\Delta H_{pp} = 20$ G). At room temperature the signal splits due to nitrogen superhyperfine coupling giving three signals of equal intensity ($\alpha_N = 5.2$ G). Further splitting due to hyperfine interaction with ^{53}Cr, $I = \frac{3}{2}$, is also observed ($\alpha_{Cr} = 5.0$ G). A similar behaviour has been recorded for other known chromium(v) *tert*-butylimido compounds.[11]

Compound **3** does not react with isocyanides or CO, but is reduced by Na/Hg in Et_2O in the presence of PhC≡CPh to green-brown solutions which failed to give crystalline products.

Cobalt and nickel complexes

The interaction of $CoCl_2(PMe_3)_3$ with 2 equivalents of $Li(p-MeC_6H_4NSPh)$ gave $Co(p-MeC_6H_4NPMe_3)_2(SPh)_2$ **4** presumably after cleavage of the N–S bond of a sulfenamido intermediate; the neutral iminophosphorane ligand $p-MeC_6H_4NPMe_3$ can be represented by the resonance forms **c** and **d**.

$$\underset{\mathbf{c}}{p\text{-}MeC_6H_4N^{-}\text{–}{}^{+}PMe_3} \longleftrightarrow \underset{\mathbf{d}}{p\text{-}MeC_6H_4{=}PMe_3}$$

The structure of **4** has been determined by X-ray diffraction, and is shown in Fig. 4; selected bond lengths and angles are given in Table 5.

The cobalt centre is in a slightly distorted tetrahedral co-

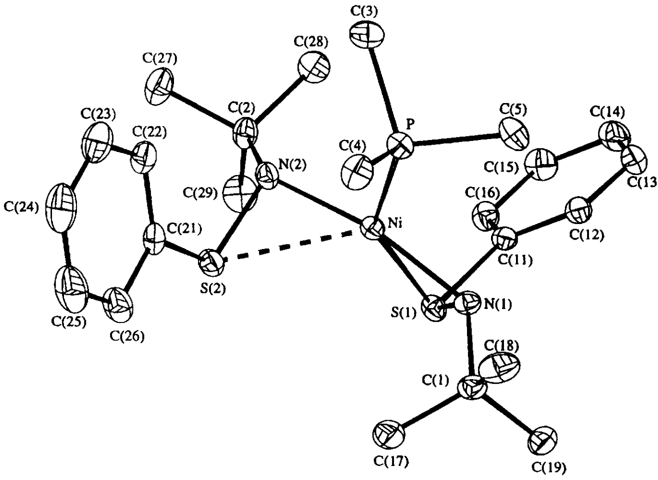


Fig. 5 The structure of Ni(η^2-Bu^{t}NSPh)$_2$(PMe$_3$) **5**, 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity

Table 6 Selected bond lengths (Å) and angles (°) for Ni(η^2-Bu^{t}NSPh)$_2$(PMe$_3$) **5** with e.s.d.s in parentheses

Ni–N(1)	1.903(2)	S(1)–N(1)	1.677(2)
Ni–N(2)	1.907(2)	S(2)–N(2)	1.688(2)
Ni–S(1)	2.216(1)	S(1)–C(11)	1.781(3)
Ni···S(2)	2.600(2)	S(2)–C(21)	1.771(3)
Ni–P	2.146(1)	N(1)–C(1)	1.502(3)
		N(2)–C(2)	1.483(3)
N(1)–Ni–N(2)	162.8(1)	P–Ni–S(1)	142.30(4)
N(1)–Ni–P	101.32(7)	N(1)–Ni–S(2)	129.06(7)
N(2)–Ni–P	95.85(7)	N(2)–Ni–S(2)	40.44(7)
N(1)–Ni–S(1)	47.29(7)	P–Ni–S(2)	111.38(3)
N(2)–Ni–S(1)	117.13(7)	S(1)–Ni–S(2)	105.75(4)
N(1)–S(1)–Ni	56.5(1)	N(2)–S(2)–Ni	47.1(1)
C(11)–S(1)–Ni	104.2(1)	C(21)–S(2)–Ni	114.0(1)
N(1)–S(1)–C(11)	102.7(1)	N(2)–S(2)–C(21)	105.1(1)
C(1)–N(1)–S(1)	114.4(2)	C(2)–N(2)–S(2)	115.7(2)
C(1)–N(1)–Ni	126.7(2)	C(2)–N(2)–Ni	127.1(2)
S(1)–N(1)–Ni	76.19(9)	S(2)–N(2)–Ni	92.5(1)

ordination sphere comprised of two benzenethiolate ligands and two p-MeC$_6$H$_4$NPMe$_3$ ligands. The bond angles around Co lie in the narrow range between 102.1(1) and 113.7(1)°. The nitrogen atoms N(1) and N(2) are accurately planar. The Co–S–C angles are 110.1(2) and 105.2(2)°, respectively. The planes of the phenyl rings are almost orthogonal [88.3(4)°] whereas the p-tolyl rings are at an angle of 36.1(2)°.

The larger contribution of the iminophosphorane resonance form **c** is indicated by careful consideration of metrical data, particularly the P–N bond length. Additionally, compound **4** shows (*i*) magnetic susceptibility at room temperature characteristic of cobalt(II) tetrahedral complexes rather than cobalt(IV) species, (*ii*) the ESR spectrum is characteristic of cobalt(II) tetrahedral complexes. Iminophosphorane complexes have been well characterised.[12] Attempts to displace the iminophosphorane with other σ donors *e.g.* PMe$_3$ or pyridine, failed. No products could be isolated after interaction of CoCl$_2$(PMe$_3$)$_3$ with Li(Bu^{t}NSPh), as above.

Interaction of NiCl$_2$(PMe$_3$)$_2$ with 2 equivalents of Li(Bu^{t}NSPh) gave the diamagnetic bis(sulfenamido) complex Ni(η^2-Bu^{t}NSPh)$_2$(PMe$_3$) **5**. The structure has been determined by X-ray diffraction and is shown in Fig. 5; selected bond lengths and angles are in Table 6. The nickel(II) complex can be described most conveniently as possessing a distorted square geometry comprised of one truly bidentate sulfenamido ligand, N(1) and S(1), a PMe$_3$ ligand and an amido nitrogen, N(2). The greatest distortions from the mean plane through Ni, S(1), P, N(1) and N(2) occur for atoms S(1) and N(1) (0.26 and −0.24 Å, respectively).

The nickel–sulfur distances, Ni–S(1) and Ni···S(2), differ significantly [2.216(1) and 2.600(2) Å, respectively]. The Ni–S(1) bond is comparatively strong, whereas the Ni···S(2) distance, 0.4 Å longer than the covalent radii sum, suggests that S(2) interacts only weakly with the metal centre. In contrast, the Ni–N bonds are equivalent within experimental error. The atoms N(1) and N(2) have shallow pyramidal geometry [with angle sums of 317.3(1) and 335.3(1)° respectively] whereas the angle sums for S(1) and S(2) are 263.5(1) and 266.3(1)°, respectively.

The Ni–P bond length [2.146(1) Å] is *ca.* 0.1 Å shorter than the sum of the covalent radii (2.25 Å), and indicates the presence of a strong P→Ni donor bond. The N–S bonds are slightly but significantly different [N(1)–S(1) 1.677(2) and N(2)–S(2) 1.688(2) Å]. The torsion angles C(11)–S(1)–N(1)–C(1) [43.1(1)°] and C(21)–S(2)–N(2)–C(2) [62.5(1)°] differ considerably. The differences noted in the structural parameters can be ascribed to the different co-ordinating behaviour for the two sulfenamido ligands.

Experimental

Analyses were by the Imperial College microanalytical laboratory. All operations were carried out under purified Ar or N$_2$, in vacuum or in a Vacuum Atmospheres glove-box. General techniques and instrumentation have been described.[13] The NMR data were obtained on a JEOL EX-270 spectrometer operating at 270 MHz (^{1}H) and referenced to the residual H impurity in the solvent (δ 7.15, C$_6$D$_6$; 5.3, CD$_2$Cl$_2$). Mass spectra were obtained using VG-7070E and VG Autospec spectrometers. Isotopic envelopes were calculated and compared with experimental patterns to good agreement. Magnetic susceptibility measurements in the solid state, at room temperature, were carried out on an Evans' balance (Sherwood Scientific, Cambridge).

Commercial chemicals were from Aldrich, Avocado and Fluka; the light petroleum used had b.p. 40–60 °C and all solvents were purified by standard methods and degassed before use. Literature procedures were used for syntheses of [Ru(η-C$_5$Me$_5$)Cl$_2$]$_2$,[14] [Cr(η-C$_5$Me$_5$)Br$_2$]$_2$,[15] CoCl$_2$(PMe$_3$)$_3$[16] and NiCl$_2$(PMe$_3$)$_2$;[17] Li(Bu^{t}NSPh) and Li(p-MeC$_6$H$_4$NSPh) were made following previously published methods.[1]

Preparation of complexes

(*N-tert*-Butylbenzenesulfenamido)chloro(η^4-1,2,3,4-tetramethylfulvene)ruthenium(II) 1 and μ-benzenethiolato-μ-*tert*-butylimido-chlorobis(η-pentamethylcyclopentadienyl)diruthenium(III) 2. To a solution of [Ru(η-C$_5$Me$_5$)Cl$_2$]$_2$ (0.31 g, 0.5 mmol) in toluene (30 cm^3) at −78 °C was added dropwise a suspension of freshly prepared Li(Bu^{t}NSPh) (0.20 g, 1.05 mmol) in toluene (30 cm^3). The mixture was allowed to reach room temperature and stirred for 12 h. Removal of volatiles under vacuum, extraction of the residue into light petroleum followed by filtration and fractional crystallisation gave compound **1** as orange crystals. Yield: *ca.* 0.05 g, 10%. Mass spectrum (EI): m/z 451 (M^+), 416 (M^+ − Cl) and 271 (M^+ − PhSNBu^t). ^{1}H NMR (C$_6$D$_6$): δ 0.28, 1.00, 1.65 and 1.75 (4 s, 12 H, C$_5$$Me_4CH_2$), 1.62 (s, 9 H, Bu^t), 4.53 and 4.74 (2 s, 2 H, C$_5$Me$_4$CH_2) and 6.78–7.17 (m, 5 H, Ph). Concentration of the supernatant and cooling to −20 °C gave **2** as red-black crystals. Yield: *ca.* 0.05 g, 15%. Mass spectrum (EI): m/z 689 (M^+), 654 (M^+ − Cl) and 519 (M^+ − C$_5$Me$_5$ + Cl). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.53 and 1.55 (2s, 30 H, 2 × C$_5$Me$_5$), 1.70 (s, 9 H, Bu^t) and 6.84–7.50 (m, 5 H, Ph).

Bis(benzenethiolato)(*tert*-butylimido)(η-pentamethylcyclopentadienyl)chromium(V) 3. To a solution of [Cr(η-C$_5$Me$_5$)Br$_2$]$_2$ (0.35 g, 0.5 mmol) in thf (30 cm^3) at − 78 °C was added dropwise a solution of Li(Bu^{t}NSPh) (0.38 g, 2.05 mmol) in thf (30 cm^3). After warming and stirring at room temperature,

Table 7 Crystal data and structure refinement details for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{20}H_{28}ClNRuS{\cdot}0.5C_6H_{14}$	$C_{30}H_{44}ClNRu_2S$	$C_{26}H_{34}CrNS_2$	$C_{32}H_{42}CoN_2P_2S_2{\cdot}C_7H_8$	$C_{23}H_{37}N_2NiPS_2$
M_r	494.10	688.31	476.66	731.80	495.35
T/K	170	150	150	120	120
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$	$P2_1/a$	$P2_1/n$
a/Å	13.628(5)	13.262(1)	9.499(5)	16.458(1)	11.159(8)
b/Å	9.159(3)	15.176(1)	24.604(10)	14.721(1)	13.240(5)
c/Å	19.392(6)	29.453(11)	10.361(5)	16.863(2)	18.103(4)
β/°	105.51(3)		95.71(4)	109.89(1)	99.97(3)
U/Å^3	2332(1)	5927(2)	2409(2)	3841	2634(2)
Z	4	8	4	4	4
D_c/Mg m^{-3}	1.407	1.543	1.314	1.265	1.249
F(000)	1028	2816	1012	1548	1056
Crystal size/mm	0.96 × 0.06 × 0.05	0.42 × 0.24 × 0.12	0.21 × 0.09 × 0.03	0.24 × 0.21 × 0.18	0.30 × 0.27 × 0.21
μ(Mo-Kα)/mm^{-1}	0.833	1.118	0.661	0.668	0.967
Collected reflections	7972	18 289	9507	15 477	11 022
Independent reflections (R_{int})	3383 (0.0618)	4314 (0.0897)	3641 (0.0811)	5955 (0.0692)	4060 (0.0567)
Correction factors	1.087, 0.862	1.151, 0.868	1.088, 0.890	1.072, 0.863	1.249, 0.888
Data, restraints, parameters	3379, 0, 259	4309, 0, 329	3637, 0, 279	5949, 0, 443	4059, 0, 271
Goodness of fit, F^2	0.992	1.157	0.612	0.916	0.969
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0431, 0.1002	0.0649, 0.1511	0.0398, 0.0651	0.0598, 0.1522	0.0389, 0.0912
(all data)	0.0586, 0.1169	0.0883, 0.1656	0.1224, 0.0858	0.0969, 0.1700	0.0497, 0.0974
Largest difference peak and hole/e Å^{-3}	1.403, −0.538	3.225, −0.829	0.301, −0.349	0.870, −0.529	1.021, −0.353

$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, $R1 = \Sigma[(F_o - F_c)]/\Sigma F_o$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + gP]$, $P = [\max(F_o^2) + 2F_c^2]/3$, where n = number of reflections, p = total number of parameters, x = 0.0464, 0.0956, 0, 0.0861, 0.0544 and g = 0 for compounds **1**, **2**, **3**, **4** and **5**, respectively.

removal of volatiles under vacuum, extraction of the residue into light petroleum (3 × 20 cm^3), followed by filtration, concentration to *ca.* 30 cm^3 and cooling to −20 °C gave purple crystals. Yield: 0.25 g, 52%. Mass spectrum (EI): m/z 476 (M^+), 367 (M^+ − SPh) and 296 (M^+ − Bu^tNSPh). For ESR data see text.

Bis(benzenethiolato)bis[trimethyl(4-methylphenylimino)-phosphorane]cobalt(II) 4. To a solution of $CoCl_2(PMe_3)_3$ (0.36 g, 1 mmol) in toluene (30 cm^3) at −78 °C was added a suspension of Li(p-MeC_6H_4NSPh) (0.47 g, 2.1 mmol) in toluene (30 cm^3). After reaching room temperature the mixture was stirred for 12 h; filtration, concentration to *ca.* 30 cm^3 and cooling to −20 °C gave the product as green crystals. Yield: 0.32 g, 45%.

Bis(*N*-*tert*-butylbenzenesulfenamido)(trimethylphosphine)-nickel(II) 5. To a solution of $NiCl_2(PMe_3)_2$ (0.28 g, 1 mmol) in toluene (30 cm^3) at −78 °C was added a suspension of Li(Bu^tNSPh) (0.39 g, 2.1 mmol) in toluene (30 cm^3). After warming and stirring for 12 h, removal of solvent under vacuum, extraction of the residue with light petroleum (3 × 20 cm^3) followed by filtration, concentration to *ca.* 30 cm^3 and cooling to −20 °C gave purple crystals. Yield: 0.22 g, 44%. NMR (C_6D_6): ^1H, δ 0.94 (d, 9 H, PMe_3), 1.14 (s, 18 H, Bu^t) and 6.96–7.72 (m, 10 H, Ph); ^{31}P, δ 14.79 (s, PMe_3),

X-Ray crystallography

X-Ray data for compounds **1**–**5** were collected at low temperature; details are listed in Table 7. A FAST TV area detector diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) was employed, as previously described.[18] The structure of compound **1** was solved using the PATT instruction of SHELXS 86,[19] those of **2**–**5** *via* direct methods procedures of the same program. The structures were refined by full-matrix least squares on F_o^2, using the program SHELXL 93.[20] All data used were corrected for Lorentz polarisation factors, and subsequently for absorption using the program DIFABS[21] with maximum and minimum correction factors (on F) listed in Table 7. The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms in compounds **1**–**5** were included in idealised positions, except for the methylene protons of **1** which were experimentally located. The hydrocarbon in the lattice of **1** originated from the solvent of crystallisation, light petroleum. The solvate molecule lies on a centre of inversion and exhibits severe disorder, hence hydrogen atom positions were not calculated. The phenyl rings of **4** exhibited some positional disorder therefore several of the carbon atoms were refined with partial occupancy in two or more sites. The solvate molecule of **4**, toluene, also exhibited disorder which was modelled as described above. Again, hydrogen atom positions were ignored.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/199.

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