DALTON

Synthesis and structure of bimetallic complexes with σ,π-bridging thienyl and benzothienyl ligands†

Angelique du Toit, Marilé Landman and Simon Lotz*

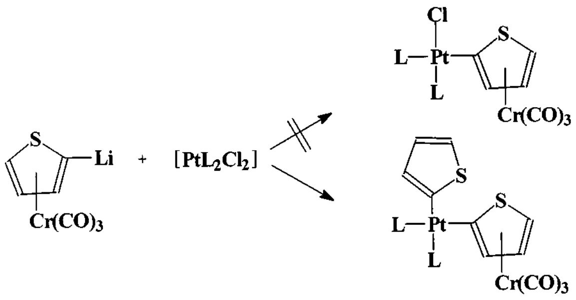
Department of Chemistry, University of Pretoria, Pretoria 0001, South Africa

The ligand properties of the organometallic fragment ($(\eta^5\text{-}SC_4H_3)Cr(CO)_3$) were studied in the new σ,π-bimetallic complexes $[Cr\{(\eta^5\text{-}SC_4H_3)PtL_2(SC_4H_3)\}(CO)_3]$ with L = CO and PMe_3 **1** or L_2 = dppe [1,2-bis(diphenylphosphino)ethane] **2**, $[Cr\{(\eta^5\text{-}SC_4H_3)Au(PPh_3)\}(CO)_3]$ **3** and $[Cr(\eta^5\text{-}SC_4H_3SnMe_3)(CO)_3]$ **4**. Whereas the intermediates $[Cr\{(\eta^5\text{-}SC_4H_3)PtL_2Cl\}(CO)_3]$ (L = PMe_3 or dppe) and $[Pt\{(SC_4H_3)Cr(CO)_3\}_2L_2]$ were too unstable to isolate and characterize, **4** slowly converted into $[Cr\{\eta^5\text{-}SC_4H_2(SnMe_3)_2\}(CO)_3]$ **5**. By contrast, the reaction of lithiated $[Cr(\eta^6\text{-}SC_8H_6)(CO)_3]$ with $[Pt(dppe)Cl_2]$ afforded the stable trinuclear complex, $[Pt\{(\eta^6\text{-}SC_8H_5)Cr(CO)_3\}_2(dppe)]$ **6**.

Studies of the activation of organic substrates by more than one transition metal in dinuclear organometallic complexes are increasingly being reported.[2] The interest in such complexes stems not only from their intriguing structural diversities[2,3] but also from their potential catalytic activity,[4] their possible importance in materials with conducting properties[5] and their role in bioinorganic chemistry.[6] Furthermore, metal–ligand activation in dinuclear complexes has not yet been studied systematically and an improved understanding of the scope and extent of such activations is very relevant. Two metals in close proximity sharing a common unsaturated ligand can co-operatively activate and assist in novel reactions, unique transformations and can cause severe structural deformations.[7] Examples are carbon–carbon bond-cleavage and coupling reactions,[8] sterically and/or electronically controlled sites of activity,[9] stabilization of reactive intermediates *via* co-ordination[1,10] and migratory movements of ligands or metal fragments.[11]

In our laboratories studies relating to heterobimetallic complexes with σ,π-bridged phenyl and thienyl ligands are of particular interest.[12] Recently we discovered an interesting activation mechanism surrounding a shared thienyl ligand which was π bonded to $Cr(CO)_3$ and σ bonded to $Mn(CO)_5$ in the 2 position. The two metal fragments irreversibly, and according to an intramolecular mechanism, exchanged σ,π co-ordination sites.[13] This novel conversion was a direct result of the metals being in electronic contact through the bridging thienyl ligand. These results prompted us further to investigate the extent of activation by σ-bonded early and late transition-metal substituents and their influence on thienyl ligands which are π bonded to $Cr(CO)_3$. In this paper we describe the synthesis and characterization of dinuclear complexes with σ-bonded platinum(II) and gold(I) fragments in the 2 position of a bridging π-co-ordinated thienyl ligand.

The platinum group metals show very high hydrodesulfurization (HDS) activity[14] and Maitlis and co-workers[15] recorded an oxidative insertion of Pt^0 into the C–S bond of thiophenes. Unfortunately for HDS purposes the reverse reaction, regenerating thiophene, is favoured. Efforts to prepare platinum(II) complexes of 2-(2-thienyl)pyridine were thwarted by metallation of a thienyl ring in the 3 position with the formation of a N,C chelate, $[Pt\{2\text{-}(SC_4H_3)C_3H_4N\}\{2\text{-}(SC_4H_4)C_5H_4N\}X]$.[16] Not many heterobimetallic complexes of the type $[M\{(\eta^6\text{-}aryl)PtL_n\}(CO)_3]$ (aryl = C_nH_{n-1}) are found in literature; the synthesis of $[Cr\{(\eta^6\text{-}p\text{-}MeC_6H_4)Pt(cod)Cl\}(CO)_3]$ (cod = cyclo-octa-1,5-diene) from aryltrimethylstannane has been known for a long time,[17] but recently the very interesting fluxional behaviour of $Pt(PPh_3)_2$ in the bimetallic Pt–Mo complex $[\{Mo(\eta^6\text{-}C_7H_6)Pt(PPh_3)_2\}(CO)_3]$ was reported.[18] To the best of our knowledge, similar σ,π-bimetallic complexes with π-co-ordinated heteroaromatic rings have not yet been recorded.



1 L = PMe$_3$, CO
2 L$_2$ = dppe

Scheme 1

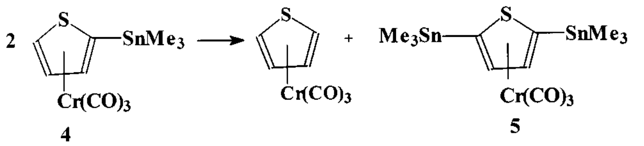
Results and Discussion

Deprotonation of thiophene in the 2 position is easily achieved in tetrahydrofuran (thf),[19] but because of the reactivity of the organolithium reagent low temperatures are essential. Higher temperatures are required for the formation of dinuclear complexes *via* salt-elimination reactions. Unfortunately, at these high temperatures the $Cr(CO)_3$ fragment is easily displaced from the σ-bonded thienyl ligand, resulting in low yields of **1** and **2**. In the reaction of 1 equivalent of $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ with *cis*-$[Pt(PMe_3)_2Cl_2]$ the expected target complex *cis*-$[Cr\{(\eta^5\text{-}SC_4H_3)Pt(PMe_3)_2Cl\}(CO)_3]$ was not obtained, but instead the novel complex **1** shown in Scheme 1 was isolated. The intermediate which formed after replacing one chloro with a thienyl ligand is highly activated and more reactive than the reactant, *cis*-$[Pt(PMe_3)_2Cl_2]$. The remaining chloro ligand of the intermediate becomes the preferred target of a second attack by the lithiated precursor. Support is found in the observation that a higher yield of **1** was obtained on using 2 equivalents of lithiated thienyl precursor. Other aspects of importance are the substitution of one of the phosphine ligands by a carbonyl ligand, the loss of one of the $Cr(CO)_3$ fragments from a thienyl moiety and the final arrangement of ligands around the platinum centre. It was concluded that PMe_3 is very substitution

---

* E-Mail: slotz@scientia.up.ac.za

† π-Hetorarene complexes. Part 5.[1]



Scheme 2

labile, and will dissociate in polar solution, thereby assisting in the substitution of $Cr(CO)_3$ from the π-bonded thienyl ligand. This was evident from the spectroscopic identification of a by-product, $[Cr(CO)_4(PMe_3)_2]$, which was isolated in very low yield.[20] To try and stabilize two phosphine ligands in *cis* positions on platinum, the reaction was repeated with the bidentate ligand dppe [1,2-bis(diphenylphosphino)ethane] instead of PMe_3. Again the expected product was not isolated and the same pattern of reactivity was observed. The formation of **2** once again emphasized the enhanced reactivity of the remaining chloro ligand. The reason for only one of the thienyl ligands being π co-ordinated to $Cr(CO)_3$ in both **1** and **2** now seems to be sterical, as it is anticipated that two π-bonded metal fragments co-ordinated next to one another in a square-planar platinum complex may be too bulky. A different behaviour was observed for σ-bonded early transition-metal substituents where the $Ti(\eta\text{-}C_5H_5)_2Cl$ fragment also contained an activated chloro ligand, but in this case it was possible to retain the second chloro ligand in the final product, $[Cr\{(\eta^5\text{-}SC_4H_3)\text{-}Ti(\eta\text{-}C_5H_5)_2Cl\}(CO)_3]$.[21] By contrast, the trimetallic complex, with both $Cr(CO)_3$ fragments present, $[Ti(\eta\text{-}C_5H_5)_2\{(\eta^5\text{-}SC_4H_3)Cr(CO)_3\}_2]$, displays pseudo-tetrahedral symmetry.

When chloro(triphenylphosphine)gold(I) was added to freshly prepared $[Cr\{(\eta^5\text{-}SC_4H_3)Li\}(CO)_3]$ in thf and the reaction mixture stirred at a low temperature the solution gradually changed to yellow-brown. On warming to room temperature excessive decomposition occurred and a brown precipitate formed. Purification afforded mainly unreacted precursor and the desired bimetallic gold compound $[Cr\{(\eta^5\text{-}SC_4H_3)\text{-}Au(PPh_3)\}(CO)_3]$ **3** in a low yield. The analogous dinuclear benzene complex $[Cr\{(\eta^6\text{-}C_6H_5)Au(PPh_3)\}(CO)_3]$[12] is of greater stability because of a much stronger π-bonded phenyl ring compared to the very labile thienyl π bond of **3**.

Higher yields of dinuclear Pt–Cr complexes were envisaged by replacing the organolithium precursor in the 2 position of the π-bonded thienyl ligand with a trimethylstannyl substituent. Added advantages are that the reaction could now be carried out in a solvent with poorer co-ordination properties, such as dichloromethane, and at higher temperatures. This procedure has successfully been applied in the past to synthesize diplatinum(II) complexes with aryl[17] and 2,5-thienylene bridges.[22] The compounds [Pt(cod)(aryl)Cl] and $[(PtL_2X)_2(\mu\text{-}2,5\text{-}SC_4H_2)]$ with $L = PBu_3$ or $L_2 = cod$ and $X = Cl$ or SC_4H_3 were prepared from the corresponding trimethyltin precursors $SnMe_3(aryl)$ and $[(SnMe_3)_2(2,5\text{-}SC_4H_2)]$, respectively, and 1 or 2 equivalents of $[Pt(cod)Cl_2]$. However, a literature survey revealed that heterocyclic organotin(IV) compounds, in which the heterocyclic group is directly bonded to tin through a ring carbon, are scarce owing to the weakness of the Sn–C bond in the heterocycle.[23] The reaction of the lithiated thienyl complex with trimethylstannyl chloride afforded two new σ,π-bimetallic complexes **4** and **5**. During the purification of **4** it became clear that this compound was constantly converting into $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ and **5**. Furthermore, the reaction of *cis*-$[PtL_2Cl_2]$ ($L = PMe_3$ or dppe) and **4** did not afford the desired Pt–Cr bimetallic complex, but yielded **5** and $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ instead. The trimethylstannyl substituent in the 2 position activates the proton in the 5 position and favours a disproportionation reaction according to Scheme 2. This method of preparation of Pt–Cr σ,π-bimetallic complexes was abandoned.

Finally, to minimize the effect of steric crowding in the Pt–Cr dinuclear complexes and to reduce the lability of the $Cr(CO)_3$ fragment, benzo[*b*]thiophene π bonded to $Cr(CO)_3$ was lithiated as described previously[24] and treated with $[Pt(dppe)Cl_2]$. Again the second chloro ligand was found to be highly activated and after an initial reaction with 1 equivalent of lithiated precursor the intermediate immediately reacted with a second molecule of lithiated precursor to yield the trimetallic complex, $[Pr\{(\eta^6\text{-}SC_8H_5)Cr(CO)_3\}_2(dppe)]$ **6**. Notable is the role of the stronger benzene–$Cr(CO)_3$ π bond which was retained for both fragments. No experimental evidence, or spectroscopic proof, was found for the formation or existence of more than one isomer which could have resulted from different orientations of the $Cr(CO)_3$ fragments with respect to the plane of the benzene rings in the compound (Fig. 1).

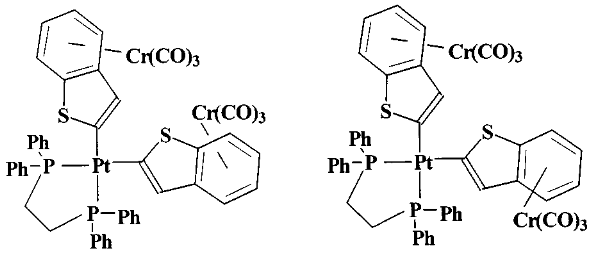


Fig. 1 Possible isomers of complex **6**

Table 1 Selected infrared spectroscopic data of the compounds in the carbonyl region in CH_2Cl_2

	$\tilde{\nu}_{CO}$ for $M(CO)_3/cm^{-1}$	
Complex	A_1	E
1[a]	1941	1844
2	1934	1839
3	1942	1848
4	1957	1874
5	1947	1850
6	1949	1866
$[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$[b]	1967	1877
$[Cr(\eta^6\text{-}SC_8H_5)(CO)_3]$[c]	1964	1866

[a] Also 2087 cm^{-1}. [b] Ref. 25. [c] Ref. 26.

Spectroscopic data reveal that the electron density on the thienyl ring increases by substituting an H of the starting compound with a late transition metal or a $SnMe_3$ fragment in the dinuclear complexes **1**–**6**. This is clearly reflected by the significant decrease in the wavenumbers in the carbonyl region of the infrared spectra of the complexes. The carbonyl vibration frequencies are listed in Table 1. Polarization of the σ bond with the negative pole in the direction of the thienyl ring and away from the metal was considered to be the main reason for increased ring electron densities of σ,π-bimetallic complexes with early transition-metal substituents, $[Cr\{(\eta^5\text{-}SC_4H_3)Ti(\eta\text{-}C_5H_5)_2X\}(CO)_3]$ ($X = Cl$, OH or SC_6H_{11}).[21] By contrast, for the electron-richer platinum and gold fragments π-back bonding from these σ-bonded metal centres *via* the bridging thienyl ligand towards the strong electron-withdrawing $Cr(CO)_3$ fragment becomes important.

Additional evidence for such an observation is found in the composition of the dinuclear complex **1** where the stronger π-acceptor ligand CO is found opposite the weakest π acceptor, *i.e.* the thienyl ligand without a $Cr(CO)_3$ fragment, thereby minimizing π competition in the square-planar complex. A further decrease in wavenumbers on going from **1** to **2** can be ascribed to the stronger π-acceptor properties of a carbonyl ligand compared to a phosphine ligand in the complexes. The infrared data of **3** reveal that $AuPPh_3$ compares roughly with $Pt(PMe_3)(CO)(SC_4H_3)$ as electron-donor substituent, but less electron density is distributed to the π-bonded thienyl ligand in **4** and **5** by one and two $SnMe_3$ substituents. The Pt–CO vibration frequency of 2087 cm^{-1} lies between the value recorded for a CO *trans* to a phenyl ligand in [Pt(PPh$_2$Me)Cl(Ph)(CO)] (ν_{CO} 2106 cm^{-1}, KBr)[27] and the cationic complex *trans*-[Pt(PEt$_3$)$_2$Ph(CO)]$^+$ (2073 cm^{-1}).[28] The carbonyl frequencies of Cr(CO)$_3$ are less affected by the Pt(dppe) fragment in **6** where the Cr(CO)$_3$ moiety is more distant and stronger bonded (η^6) to the benzene of the benzothienyl ligand.

Molecular ion peaks were observed for complexes **2**, **4** and **5** in the mass spectra obtained from electron-impact studies. Comparison of the spectra of **1** (peak of highest *m*/*z* value is 649 which corresponds to $M^+ - 3CO$) and **2** made recognition of a certain trend possible. After initial fragmentation of three carbonyl ligands, the fragmentation of the π-co-ordinated Cr from the thienyl ligand precedes the rupture of the Pt–C σ bond. Both spectra show a principal ion with *m*/*z* values corresponding to the fragment ion Pt(phosphine)$_2^+$, and also reveal the formation of the bithiophene monocation (*m*/*z* = 166) in the spectrometer. By contrast, the SnMe$_3$ substituent is fragmented earlier, *i.e.* before the rupture of the Cr–thienyl π-bond, in the spectra of **4** and **5**. The principal ion in **4** has a *m*/*z* value (136) corresponding to the fragment ion Cr(η^5-SC$_4$H$_4$)$^+$. Especially noteworthy is a peak with *m*/*z* value corresponding to the ion of the starting complex Cr(η^5-SC$_4$H$_4$)(CO)$_3^+$ with the carbonyl ligands still intact. Normally organometallic complexes will lose carbonyl ligands first. Furthermore, the starting complex [Cr(η^5-SC$_4$H$_4$)(CO)$_3$] is also one of the products of the disproportionation reaction of **4** in solution.

Improved resolution of the proton resonances in the NMR spectra of the bimetallic complexes was obtained by recording spectra at low temperatures and in different deuteriated solvents (Table 2; see Experimental section for additional information). The high-field shifts of π-complexed thiophene protons have been explained in terms of the role of Cr(CO)$_3$ in the withdrawal of electron density from the ring, the magnetic anisotropic effect exerted on the ring and the suppression of the ring current as the result of localization of the double bonds during co-ordination.[29] The protons of both the σ- and π-co-ordinated thienyl rings display a typical ABC pattern, with H^5 less shielded and at highest δ value for **1**, **2** and **4**. However, in **3** H^4 is further downfield from H^5, presumably because of the strong electron-shielding effect of the electron-rich Au.

The chemical shift of the proton closest to Pt in complexes **1** and **2** is observed at highest field and displays the biggest $^3J_{PtH}$ coupling. Owing to the relatively strong platinum satellites the peak for H^3 is broad and $^3J_{HH}$ was not observed on the CD$_2$Cl$_2$ ^{1}H NMR spectrum of **1**. The protons of the π-bonded thienyl display smaller coupling constants with Pt compared to those of the σ-bonded thienyl ligand. The chemical shifts of the σ-thienyl and dppe ligands overlap and could only be resolved by conducting a COSY (correlation spectroscopy) experiment. For both **1** and **2** the chemical shifts of H^4 and H^5 are closer together for the π- than the σ-bonded thienyl ligand. The resonances of the thienyl protons, H^3–H^5, are solvent dependent but retain their different positions in the spectra. The chemical shifts of the ring protons are shifted to lower field in [^{2}H$_6$]acetone compared to those in [^{2}H$_2$]dichloromethane for **1** and [^{2}H$_1$]chloroform for **2**. This effect was also observed for the precursor [Cr(η^5-SC$_4$H$_4$)(CO)$_3$] by Mangini and Taddei[30] and was attributed to hydrogen bonding between the thiophene protons and the carbonyl group of acetone. The ^{1}H NMR spectrum of **2** shows ten resonances for the phenyl protons of dppe with the four *ortho* protons downfield from the *meta* and *para* protons. The two methylene groups show an ABCD pattern, which confirms that the dppe-ligand is not flat in the square-planar platinum(II) complexes, but that the two methylene groups protrude above and below the plane of the complex. On comparing chemical shifts of the thienyl protons in **4** and **5**, the protons in **5** are observed more downfield than the corresponding protons of **4**. This can be ascribed to the replacement of a H by a second SnMe$_3$ in the 5 position and the resulting accumulating inductive effect of the methyl groups on the second SnMe$_3$ moiety. On comparing the ^{1}H NMR spectra of SnMe$_3$(2-SC$_4$H$_3$)[31] and [(SnMe$_3$)$_2$(2,5-SC$_4$H$_2$)][32] the chemical shifts are also downfield from those of free thiophene as is the case for **4** and **5** compared to [Cr(η^5-SC$_4$H$_4$)(CO)$_3$], again demonstrating the deshielding effect of a SnMe$_3$ moiety and the shielding effect of π co-ordination to Cr. The expected singlet for H^3 and H$^{3'}$ in **6** was not observed and is probably obscured by the multiplet assigned to the phenyl protons.

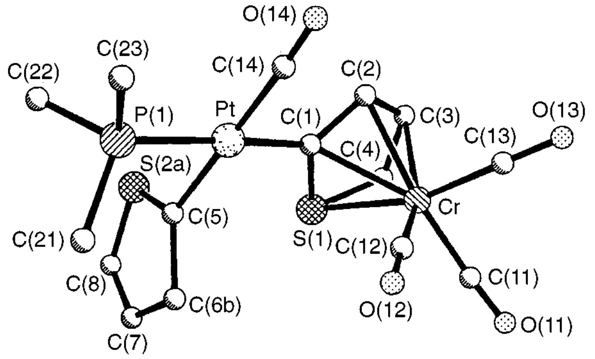


Fig. 2 Molecular structure and crystallographic numbering scheme for complex **1**

The chemical shifts of the carbonyl resonances of Cr(CO)$_3$ in the ^{13}C NMR spectra are solvent independent and practically the same for complexes **1**–**5** (δ 234–236). These values correspond well with literature values[33] and demonstrate their insensitivity to substituents on the π-bonded thienyl ring. In fact, co-ordination to the benzene fragment of benzo[*b*]thienyl in **6** affords a similar chemical shift value of *δ* 235.6. For Pt–CO in **1** a doublet is found with a small $^2J_{PC}$ coupling (3.32 Hz) and the chemical shift δ 182.0 corresponds well with literature values.[33] The chemical shift recorded for *trans*-[Pt(AsMe$_3$)$_2$(CO)Me]$^+$ was δ 178.7.[34] The relative positions of the chemical shifts for the carbons correspond to that of the protons in both the σ- and π-co-ordinated thienyl ligands. The chemical shift of the *ipso*-carbon of the σ-co-ordinated thienyl ligand opposite the CO ligand in **1** is observed more downfield compared to the value recorded for *cis*-[Pt(2-SC$_4$H$_3$)$_2$(PBu$_3$)$_2$].[22] In the ^{13}C NMR spectrum of **5** only two signals are observed for the thienyl carbons representing (*i*) the two equivalent *ipso*-carbons, C^2 and C^5, and (*ii*) the two unsubstituted carbons C^3 and C^4. Similarly, the downfield shifts of the *ipso*-carbons of thienyltin compounds were ascribed by Doddrell *et al.*[35] to inductive effects. The chemical shift of the *ipso*-carbon of the thienyl ligand in **3** was not observed. Based on the fact that the resonance at δ 92.3 ($^3J_{PC}$ = 3.0) displays a greater P–C coupling constant than the shift at δ 101.7 ($^3J_{PC}$ = 2.7), C^4 and C^5 could be assigned.

From the ^{31}P NMR spectrum of complex **6** it is apparent that the compound contains two identical ligands *trans* to the phosphines of dppe, since only one signal was observed. By contrast, two signals are observed for **2**. A *trans* influence based on π competition will be greater for the thienyl ligand π bonded to Cr(CO)$_3$ than for the σ-bonded thienyl ligand. A higher coupling constant, $^1J_{PtP}$, will correlate with a poorer π-acceptor ligand in the *trans* position.[36]

To confirm conclusions drawn from the spectroscopic data and seeing that no single-crystal structure determination of a σ,π-bridged thienyl ligand with a π-co-ordinated Cr(CO)$_3$ and a σ-bonded PtL$_2$X fragment had been recorded before, a structure determination of complex **1** was performed. A perspective view of the molecular geometry is depicted in Fig. 2, together with the atom-numbering scheme. Selected bond lengths and angles are listed in Table 3. The thiophene ring co-ordinated to Cr is planar and the ring carbons are equidistant from Cr indicating a η^5 co-ordination mode. The Cr–C (ring) bond distances range from 2.18(1) to 2.25(1) Å, and the Cr–S distance is 2.370(3) Å. These values correspond well with structural data

Table 2 The NMR data of the complexes: chemical shifts[a] (δ) and coupling constants *J*/Hz

		^{1}H NMR			^{13}C NMR				
Complex	Ring position	η-Thienyl	κ-Thienyl	Other	Carbonyls	η-Thienyl	κ-Thienyl	Other	^{31}P NMR
1[b]				PMe_3	236.7 (CrCO)			PMe_3	PMe_3
	3	5.43 (d, $^{3}J_{\mathrm{HH}}$ 3.0)	6.85 (d,[c,d] $^{3}J_{\mathrm{HH}} \approx 3.8$, $^{3}J_{\mathrm{PtH}}$ 36.4)	1.47 (d,[d] $^{2}J_{\mathrm{PH}}$ 10.8, $^{3}J_{\mathrm{PtH}}$ 38.3)	182.0 (d, PtCO, $^{2}J_{\mathrm{PC}}$ 3.3)	97.8 (d,[d] $^{3}J_{\mathrm{PC}}$ 7.7, $^{2}J_{\mathrm{PtC}}$ 55.5)	128 (s,[d] $^{2}J_{\mathrm{PtC}}$ 69.4)	14.6 (d,[d] $^{1}J_{\mathrm{PC}}$ 39.0, $^{2}J_{\mathrm{PtC}}$ 33.6)	−23.2 (s,[d] $^{1}J_{\mathrm{PtP}}$ 1992)
	4	5.61 (t, $^{3}J_{\mathrm{HH}}$ 3.0)	7.16 (t)			94.7 (d,[d] $^{4}J_{\mathrm{PC}}$ 2.4, $^{3}J_{\mathrm{PtC}}$ 49.9)	128.2 (s,[d] $^{3}J_{\mathrm{PtC}}$ 48.6)		
	5	5.64 (d, $^{3}J_{\mathrm{HH}}$ 1.9)	7.60 (d, $^{3}J_{\mathrm{HH}}$ 4.8, $^{4}J_{\mathrm{PtH}}$ 21.0)			105.9 (d,[d] $^{4}J_{\mathrm{PC}}$ 4.5, $^{3}J_{\mathrm{PtC}}$ 58.2)	132.2 (d,[d] $^{4}J_{\mathrm{PC}}$ 4.2, $^{3}J_{\mathrm{PtC}}$ 47.9)		
	2					110.0	143.0		
2				dppe	236.6			dppe	dppe
	3	4.90 (dd,[d] $^{4}J_{\mathrm{PH}}$ 0.7, $^{3}J_{\mathrm{HH}}$ 2.8, $^{3}J_{\mathrm{PtH}}$ 27.8)	6.91 (ddd, $^{4}J_{\mathrm{HH}}$ 1.3, $^{4}J_{\mathrm{PH}}$ 3.4, $^{3}J_{\mathrm{HH}}$ 4.6)	8.05 (ddd, *o,o′*, $^{4}J_{\mathrm{HH}}$ 1.9, $^{3}J_{\mathrm{HH}}$ 8.6, $^{3}J_{\mathrm{PH}}$ 10.4)		98.6 (d,[d] $^{3}J_{\mathrm{PC}}$ 8.0, $^{2}J_{\mathrm{PtC}}$ 56.2)	127.5	133.7–135.0 (*o*-C)	44.7 (s,[d] $^{1}J_{\mathrm{PtP}}$ 2117.9)
	4	5.47 (td,[d] $^{5}J_{\mathrm{PH}}$ 1.4, $^{3}J_{\mathrm{HH}}$ 3.4, $^{4}J_{\mathrm{PtH}}$ 10.3)	7.53 (dd, $^{3}J_{\mathrm{HH}}$ 7.5, $^{3}J_{\mathrm{HH}}$ 1.9)	7.99 (ddd, *o,o′*, $^{4}J_{\mathrm{HH}}$ 1.9, $^{3}J_{\mathrm{HH}}$ 8.7, $^{3}J_{\mathrm{PH}}$ 10.7)		94.7 (s,[d] J_{PtC} 52.8)	131.3	129.4–132.6 (*m*-C)	42.2 (s,[d] $^{1}J_{\mathrm{PtP}}$ 2232.8)
	5	5.58 (dd,[d] $^{3}J_{\mathrm{HH}}$ 3.7, $^{5}J_{\mathrm{PH}}$ 0.7, $^{4}J_{\mathrm{PtH}}$ 13.1)	7.65[c]	7.83 (ddd, *o,o′*, $^{4}J_{\mathrm{HH}}$ 1.3, $^{3}J_{\mathrm{HH}}$ 8.3, $^{3}J_{\mathrm{PH}}$ 11.5)		107.0 (dd,[d] $^{4}J_{\mathrm{PC}}$ 4.8, $^{4}J_{\mathrm{PC}}$ 9.6, $^{3}J_{\mathrm{PtC}}$ 48.2)	132.1	128.5–129.0 (*p*-C)	
				7.67[c] (ddd, *o,o′*), 7.73–7.69 (8 H, *m,m′*), 7.27 (td, *p,p′*, $^{4}J_{\mathrm{HH}}$ 1.2, $^{3}J_{\mathrm{HH}}$ 8.3, $^{3}J_{\mathrm{HH}}$ 11), 2.13–2.58 (*m,m′*)		n.o.[e]		30.2 (CH_2)	
3[f]				PPh_3				PPh_3	
	3	5.60 (dd, $^{4}J_{\mathrm{PH}}$ 2.0, $^{3}J_{\mathrm{HH}}$ 4.4)		7.39–7.71 (m)	236.0	95.5 (d, $^{3}J_{\mathrm{PC}}$ 4.9)		129.1 (d, *o*-C, $^{2}J_{\mathrm{PC}}$ 4.5) 129.2 (d, *o*-C, $^{2}J_{\mathrm{PC}}$ 3.8) 133.9 (*m*-C), 134.1 (*m*-C), 132.0 (*p*-C)	
	4	5.86 (t, $^{3}J_{\mathrm{HH}}$ 3.2)				92.3 (d, $^{4}J_{\mathrm{PC}}$ 3.0)			
	5	5.77 (d, $^{3}J_{\mathrm{HH}}$ 3.2)				101.7 (d, $^{4}J_{\mathrm{PC}}$ 2.7)			
	2					n.o.			
4				$SnMe_3$					
	3	5.97 (dd, $^{4}J_{\mathrm{HH}}$ 1.5, $^{3}J_{\mathrm{HH}}$ 2.8)		0.31 (s,[g] $^{2}J_{\mathrm{SnH}}$ 62)	234.4	90.2		−5.4	
	4	6.00 (t, $^{3}J_{\mathrm{HH}}$ 2.2)				94.2			
	5	6.03 (d, $^{3}J_{\mathrm{HH}}$ 2.2)				104.7			
	2					119.1			
5				$SnMe_3$				$SnMe_3$	
		6.03 (s,[g] $^{3}J_{\mathrm{SnH}}$ 9.6, $^{4}J_{\mathrm{SnH}}$ 2.8)		0.40 (s,[g] $^{2}J_{\mathrm{SnH}}$ 59.9)	235.3	90.2, 94.3		−7.3	
6[f]		η-C_6H_4		dppe		η-C_6H_4		dppe	
		5.78 (d, $^{3}J_{\mathrm{HH}}$ 6.5), 5.04 (dd, $^{3}J_{\mathrm{HH}}$ 6.5, $^{3}J_{\mathrm{HH}}$ 6.0), 5.12 (dd, $^{3}J_{\mathrm{HH}}$ 6.5, $^{3}J_{\mathrm{HH}}$ 6.0), 6.02 (d, $^{3}J_{\mathrm{HH}}$ 6.2)	n.o. (H^3)	2.33, 7.40–7.50 (m)	235.6	89.4 ($C^{4,4'}$), 90.3 ($C^{5,5'}$), 91.1 ($C^{6,6'}$), 105.8 ($C^{9,9'}$), n.o. ($C^{8,8}$)	151.1 ($C^{2,2'}$), 125.0 ($C^{3,3'}$)	134.2 (*ipso*-C), 134.3 (*o*-C), 129.8 (*m*-C), 132.2 (*p*-C) CH_2 30.6	44.5 ($^{1}J_{\mathrm{PtP}}$ 2072)

[a] Spectra recorded at −10 °C in $(CD_3)_2CO$ as solvent unless stated otherwise. [b] Solvent CD_2Cl_2. [c] Presumably a doublet. [d] Platinum satellites. [e] n.o. = Not observed. [f] Solvent $CDCl_3$. [g] Tin satellites.

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Pt–C(1)	2.067(10)	S(1)–C(1)	1.744(11)
Pt–C(5)	2.054(9)	S(1)–C(4)	1.725(13)
Pt–C(14)	1.890(10)	C(1)–C(2)	1.421(15)
Pt–P(1)	2.311(3)	C(2)–C(3)	1.423(17)
Cr–S(1)	2.370(3)	C(3)–C(4)	1.395(20)
Cr–C(1)	2.245(8)	S(2a)–C(5)	1.675(8)
Cr–C(2)	2.226(10)	S(2a)–C(8)	1.665(17)
Cr–C(3)	2.227(12)	C(5)–C(6b)	1.579(11)
Cr–C(4)	2.184(11)	C(5)–S(2b)	1.579(11)
Cr–C(11)	1.844(13)	C(6b)–C(7)	1.579(16)
Cr–C(12)	1.813(12)	C(7)–C(8)	1.343(18)
Cr–C(13)	1.802(11)		

C(1)–Pt–C(5)	88.2(4)	S(1)–C(4)–C(3)	111.5(9)
C(1)–Pt–C(14)	91.9(4)	C(5)–S(2a)–C(8)	94.4(6)
C(5)–Pt–C(14)	179.4(4)	Pt–C(5)–S(2a)	122.1(5)
C(1)–Pt–P(1)	174.9(3)	Pt–C(5)–C(6b)	122.3(5)
C(5)–Pt–P(1)	86.9(3)	S(2a)–C(5)–C(6b)	115.4(6)
C(14)–Pt–P(1)	92.9(3)	C(5)–C(6b)–C(7)	98.7(7)
C(11)–Cr–C(13)	87.7(5)	C(6b)–C(7)–C(8)	116.8(12)
C(12)–Cr–C(13)	87.5(5)	S(2a)–C(8)–C(7)	114.6(11)
C(1)–S(1)–C(4)	93.6(6)	C(21)–P(1)–C(22)	105.4(6)
S(1)–C(1)–C(2)	108.3(8)	C(22)–P(1)–C(23)	105.5(6)
C(1)–C(2)–C(3)	114.6(10)	C(21)–P(1)–C(23)	103.4(7)
C(2)–C(3)–C(4)	111.6(11)		

reported for $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$,[37] but the Cr–S distance in **1** is slightly longer. The three carbonyl ligands co-ordinated to Cr form a tripod with the ring. This is in accordance with the very well known piano-stool conformation of arenechromium complexes.[38] Furthermore, the thiophene sulfur atom is found in a position *trans* to one of the carbonyls. Owing to the large standard deviations in the C–C bond lengths of the thienyl rings, it is impossible to draw conclusions from these data. The σ-bonded thienyl ligand is disordered in two sites related by a 180° rotation (see Experimental section). Severe distortion was also found for $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$, which revealed a three-fold orientational disorder.[37] It was anticipated that the Pt–C (thienyl) bond *trans* to CO would be longer. On the contrary, both Pt–C (thienyl) bond lengths [2.054(9) and 2.067(10) Å] are the same, within experimental error, and are comparable to the Pt–C(sp^2) single-bond distances recorded for $[Pt(CO_2H)(C_6H_5)(PEt_3)_2]$,[27] *cis*-$[Pt(o\text{-}MeC_6H_4)_2(PEt_3)_2]$[39] and the bimetallic ferrocenyl compound $[Pt(PPh_3)_2(p\text{-}C_6H_5CO_2Me)(CCR)]$[40] (R = ferrocenyl) of 2.058, 2.091 and 2.070 Å, respectively. There is a slight distortion of the square-planar geometry around the platinum. The phosphine and π-co-ordinated thiophene are slightly bent towards each other at a C(1)–Pt–P(1) angle of 174.9(3)°. The distortion is also visible in the P(1)–Pt–C(5) angle [86.9(3)°] and to a lesser extent in the C(1)–Pt–C(5) angle [88.2(4)°]. This is unexpected since the three ligands involved represent the three bulkiest in the complex.

In conclusion, the $(\eta^5\text{-}SC_4H_3)Cr(CO)_3$ substituent displays π-acceptor properties and is reasonably bulky. It activates the remaining chloro ligand in complexes of the type $[PtL_2\{(\eta^5\text{-}SC_4H_3)Cr(CO)_3\}Cl]$ to such an extent that the chloro ligand is immediately displaced by a second $(\eta^5\text{-}SC_4H_3)Cr(CO)_3$ ligand. However, owing to the bulkiness of these metal-containing ligands, one of the $Cr(CO)_3$ fragments is decomplexed and absent in the final square-planar platinum complexes.

Experimental

All reactions were performed under an inert atmosphere using standard Schlenk-tube techniques.[41] Solvents were dried by the usual procedures and distilled under nitrogen prior to use.[42] The reagents $SnMe_3Cl$, dppe, cod, LiBu and benzo[*b*]thiophene were used as purchased from Aldrich. Thiophene[43] was purified before use; PMe_3[44] prepared as described previously. The starting complexes were prepared according to literature methods: $[Pt(PMe_3)_2Cl_2]$,[45] $[Pt(dppe)Cl_2]$,[46] $[Pt(cod)Cl_2]$,[47] $[Au(PPh_3)Cl]$,[48] $[Cr(NH_3)_3(CO)_3]$,[49] $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$,[25] $[Cr(\eta^6\text{-}SC_8H_5)(CO)_3]$.[26] Column chromatography was performed on silica gel (0.063–0.200 mm) and the column cooled by recycling (−20 °C) Pr^iOH through the column jacket. Nuclear magnetic resonance (NMR) spectra were recorded at −20 °C on a Bruker AC-300 spectrometer at 300.135 (^1H), 75.469 (^{13}C) and 121.496 MHz (^{31}P), respectively. Proton and carbon-13 chemical shifts are positive to high frequency of $SiMe_4$ and the signals of the deuteriated solvents were used as reference (internal); phosphorus-31 chemical shifts are positive to high frequency of 85% H_3PO_4 (external). The NMR solvents were degassed by several freeze–pump–thaw cycles, and sample tubes were sealed under nitrogen. Infrared spectra were recorded as liquid solutions on a Bomem Michelson-100 FT spectrophotometer, and frequencies were assigned relative to a polystyrene standard. Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument operating at 70 eV (*ca.* 1.12×10^{-17} J). Elemental analyses were obtained from the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria, South Africa.

Preparations

$[Cr\{(\eta^5\text{-}SC_4H_3)Pt(PMe_3)(CO)(SC_4H_3)\}(CO)_3]$ 1. The dropwise addition of a 1.6 mol dm^{-3} hexane solution (1.0 cm^3) of LiBu (1.6 mmol) to a cooled, −50 °C, thf solution (15 cm^3) containing $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ (0.32 g, 1.45 mmol) afforded the lithiated thienyl complex in high yield after 30 min. Addition of *cis*-$[Pt(PMe_3)_2Cl_2]$ (0.57 g, 1.36 mmol) in small portions over 10 min resulted in a gradual change from orange-red to yellow and eventually dark red-brown. The mixture was stirred at −30 °C for 30 min and then left to stir in the cold overnight and slowly warmed to room temperature. The solvents were removed under reduced pressure and the brown residue dissolved in dichloromethane and filtered through silica gel. Again the solvent was removed and products were purified using column chromatography. Initially hexane was used as eluent and then the polarity of the eluent was increased to a 2:1 ratio of hexane and dichloromethane. Two fractions were removed from the column. The first, yellow-orange, was identified as $[Cr\{(\eta^5\text{-}SC_4H_3)Pt(PMe_3)(CO)(SC_4H_3)\}(CO)_3]$ **1** (0.085 g, 11% based on Pt) and the second was the starting compound $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ (0.13 g, 43%). The yield of **1** was increased to 0.16 g (20%) by using 2 equivalents of $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ (Found: C, 30.57; H, 2.79. $C_{15}H_{15}CrO_4PPtS_2$ requires C, 29.95; H, 2.51%). Mass spectrum (M^+ not observed): *m*/*z* 517 (M^+ −3CO, 14), 513 $[Pt(SC_4H_3)_2(PMe_3)_2{}^+$, 18], 430 $[Pt(SC_4H_3)(PMe_3)_2{}^+$, 4], 347 $[Pt(PMe_3)_2{}^+$, 47], 299 $[Pt(PMe_3)(CO)^+$, 4] and 166 $[(SC_4H_3)_2{}^+$, 26%]. ^1H NMR [$(CD_3)_2CO$, 0 °C]: δ 6.83 (d, H^3, $^3J_{HH} = 3.9$, platinum satellites, $^3J_{PtH} = 37.2$), 7.17 (td, H^4, $^3J_{HH} = 3.9$, $^5J_{PH} = 0.9$), 7.69 (d, H^5, $^3J_{HH} = 4.2$), 5.82, 5.79 (m, η-thienyl, H^3–H^5) and 1.60 (d, 9 H, $^2J_{PH} = 11.2$, platinum satellites, $^3J_{PtH} = 38.7$ Hz); see also Table 2.

$[Cr\{(\eta^5\text{-}SC_4H_3)Pt(dppe)(SC_4H_3)\}(CO)_3]$ 2. The compound $[Pt(dppe)Cl_2]$ (1.02 g, 1.54 mmol) was added to freshly prepared $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ (0.34 g, 1.55 mmol) in thf (30 cm^3) at −90 °C. The orange-red solution turned orange-brown with addition of the platinum complex. The mixture was stirred at −90 °C for 1 h and then allowed to warm to −60 °C. The reaction was monitored by thin-layer chromatography, while the mixture was gradually allowed to warm up. As soon as it was clear that the reaction had proceeded to completion and decomposition started to set in, the reaction mixture was removed from the cold and stirred at room temperature for 30 min. The solvents were removed under reduced pressure and the reaction mixture was purified by column chromatography. A non-polar solvent (hexane) was used as eluent initially and as soon as separation could be seen on the column the polarity of the eluent was gradually increased to a 1:1 ratio of hexane and dichloromethane. Two fractions were removed from the column, the first, yellow-orange, afforded $[Cr\{(\eta^5\text{-}SC_4H_3)Pt(dppe)(SC_4H_3)\}(CO)_3]$ **2** (0.18 g, 13% based on Pt) and the second the starting compound $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ (0.32 g, 47%). The yield of **2** was increased to 0.27 g or 20% by using 2 equivalents of $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ (Found: C, 49.97; H, 3.62. $C_{37}H_{30}CrO_3P_2PtS_2$ requires C, 49.61; H, 3.38%). Mass spectrum: *m/z* 895 (M^+ based on ^{195}Pt isotope, 1), 811 ($M^+ - 3CO$, 45), 759 $[Pt(SC_4H_3)_2(dppe)^+$, 20], 676 $[Pt(SC_4H_3)(dppe)^+$, 7], 593 $[Pt(dppe)^+$, 98%] and 166 $[(SC_4H_3)_2{}^+$, 28%]. NMR ($CDCl_3$, −10 °C): ^1H, δ 6.42 (ddd, H^3, $^4J_{HH} = 0.9$, $^3J_{HH} = 3.2$, platinum satellites, $^3J_{PtH} = 38.1$), 7.42 (m, H^4), 7.54 (m, H^5), 4.83 (t, H^3, $^3J_{HH} = 2.2$, platinum satellites, $^3J_{PtH} = 26.5$), 5.15 (t, H^4, $^3J_{HH} = 2.8$), 5.29 (d, H^5, $^3J_{HH} = 3.2$), 8.03 (dd, 2 H, *o,o′*, $^4J_{HH} = 2.2$, $^3J_{HH} = 8.3$), 7.88 (dd, 2 H, *o,o′*, $^4J_{HH} = 2.2$, $^3J_{HH} = 7.8$), 7.89 (dd, 2 H, *o,o′*, $^4J_{HH} = 2.9$, $^3J_{HH} = 7.7$), 7.61 (dd, 2 H, *o,o′*), 7.3–7.6 (dd, 8 H, *m,m′*), 7.20 (dd, 2 H, *p,p′*, $^4J_{HH} = 1.8$, $^3J_{HH} = 7.5$), 6.94 (dd, 2 H, *p,p′*), 1.81–2.78 (m, 4 H, CH_2); ^{13}C, δ 236.4 (Cr–CO), 127.2 (C^3), 130.6 (C^4), 131.1 (C^5), C^2 not observed; 98.0 (d, C^3, $^3J_{PC} = 7.5$, platinum satellites, $^2J_{PtC} = 56.2$), 93.5 (s, C^4, platinum satellites, $^3J_{PtC} = 24.0$), 106.1 (dd, C^5, $^4J_{PtC} = 5.2$, $^4J_{PC} = 9.6$, platinum satellites, $^3J_{PtC} = 51.4$), C^2 not observed; 131–135.0 (*o*-C), 127.5–129.7 (*m*-C, *p*-C), 29.9 (CH_2); ^{31}P, δ 44.7 (s, platinum satellites, $^1J_{PtP} = 2116.9$) and 42.2 (s, platinum satellites, $^1J_{PtP} = 2232.8$ Hz); see also Table 2.

$[Cr\{(\eta^5\text{-}SC_4H_3)Au(PPh_3)\}(CO)_3]$ 3. The compound $[Au(PPh_3)Cl]$ (1.05 g, 2.10 mmol) was added to freshly prepared $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ (0.46 g, 2.10 mmol) in thf (30 cm^3) at −90 °C to afford an orange-brown reaction mixture. The mixture was stirred at −90 °C for 30 min and allowed gradually to warm to −70 °C from where the reaction was monitored by TLC. As soon as it was evident that the reaction was not proceeding towards the formation of new complexes, the reaction mixture was removed from the cold and stirred at room temperature for 30 min. The solvents were removed under reduced pressure and the reaction mixture was purified by column chromatography. The column was eluted and the separation successfully accomplished by a 1 : 1 ratio of hexane and dichloromethane. Two fractions were removed from the column; the first, orange-red, affording $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ (0.16 g, 35%) and the second, yellow, giving $[Cr\{(\eta^5\text{-}SC_4H_3)Au(PPh_3)\}(CO)_3]$ **3** (0.13 g, 9%) (Found: C, 44.57; H, 2.99. $C_{25}H_{18}AuCrO_3PS$ requires C, 44.26; H, 2.67%). Mass spectrum: no M^+ observed.

$[Cr(\eta^5\text{-}SC_4H_3SnMe_3)(CO)_3]$ 4 and $[Cr\{\eta^5\text{-}SC_4H_2(SnMe_3)_2\}(CO)_3]$ 5. Trimethylstannyl chloride (0.55 g, 2.79 mmol) was added to freshly prepared $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ (0.55 g, 2.48 mmol) in thf (30 cm^3) at −90 °C. The orange-red reaction mixture changed to yellow-brown. After the mixture was stirred at −90 °C for 10 min it was allowed gradually to warm to −70 °C, where two new yellow complexes could be seen by TLC. Stirring was continued until it was evident that the reaction had proceeded to completion and decomposition started to set in. The mixture was removed from the cold and stirred at room temperature for 30 min. The solvents were removed under reduced pressure and the reaction mixture was purified using column chromatography. Initially hexane was used as eluent and then the polarity of the eluent was increased with dichloromethane up to a 1 : 1 ratio. Three fractions were removed from the column in order of increasing polarity. First, a yellow fraction affording $[Cr(\eta^5\text{-}SC_4H_3SnMe_3)(CO)_3]$ **4** (0.84 g, 62%) was collected. The second yellow fraction yielded $[Cr\{\eta^5\text{-}SC_4H_2(SnMe_3)_2\}(CO)_3]$ **5** (0.26 g, 27%) and the third was identified as unreacted starting material, $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$ (0.044 g, 8%). In polar solvents such as thf **4** converted into **5** and $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3]$.

Complex **4** (Found: C, 31.57; H, 3.59. $C_{10}H_{12}CrO_3SSn$ requires C, 31.36; H, 3.16%): mass spectrum *m/z* 383 (M^+, 18), 327 ($M^+ - 2CO$, 2), 299 ($M^+ - 3CO$, 15), 269 ($CrSnC_5H_6S^+$, 5), 254 ($CrSnC_4H_3S^+$, 1), 220 $[Cr(\eta^5\text{-}SC_4H_4)(CO)_3{}^+$, 3] and 136 $[Cr(\eta^5\text{-}SC_4H_4)^+$, 100%]; NMR ($CDCl_3$, −10 °C), ^1H, δ 5.40 (d, H^3, $^3J_{HH} = 2.3$), 5.60 (t, H^4, $^3J_{HH} = 2.4$), 5.66 (d, H^5, $^3J_{HH} = 2.4$), 0.39 (s, 9 H, tin satellites, $^2J_{SnH} = 56.6$ Hz); ^{13}C, δ 234.2 (Cr–CO), 86.2 (C^3), 91.5 (C^4), 102.5 (C^5), 122.2 (C^2) and −7.2 (3 C); see also Table 2.

Table 4 Crystallographic data for complex **1**

Empirical formula	$C_{15}H_{15}CrO_4PPtS_2$
Space group	$P\bar{1}$
a/Å	6.427(1)
b/Å	11.631(3)
c/Å	13.414(4)
α/°	102.57(2)
β/°	97.75(2)
γ/°	95.94(2)
U/Å^3	967
Z	2
F(000)	572
D_c/g cm^{-3}	2.06
μ(Mo-Kα)/cm^{-1}	81.5
2θ Range/°	13–26
No. reflections measured	3712
No. unique reflections	3388
No. observed reflections [$I > 3.0\sigma(I)$]	2797
No. variables	218
R,^{a} *R′*^{b}	0.0376, 0.0405

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$; $w^{-1} = \sigma^2(F_o) + 0.000\,091\,5(F_o{}^2)$.

Complex **5** (Found: C, 28.87; H, 3.81. $C_{13}H_{20}CrO_3SSn_2$ requires C, 28.61; H, 3.69%); mass spectrum *m/z* 546 (M^+, 2), 490 ($M - 2CO$, 2), 462 ($M^+ - 3CO$, 12), 432 ($CrSn_2C_8H_{15}S^+$, 3), 299 ($CrSnC_7H_{12}S^+$, 1), 286 ($CrSnC_6H_9S^+$, 1), 269 ($CrSnC_5H_6S^+$, 1), 254 ($CrSnC_4H_3S^+$, 1) and 136 $[Cr(\eta^5\text{-}SC_4H_4)^+$, 6%]; NMR ($CDCl_3$, −10 °C), ^1H, δ 5.59 (s, br, 2 H), 0.39 (s, 18 H, tin satellites, $^2J_{SnH} = 56.9$); ^{13}C, δ 234.2 (Cr–CO), 91.5, 99.8, −7.2 (s, tin satellites, $^1J_{SnC} = 373$ Hz); see also Table 2.

$[Pt\{(\eta^6\text{-}SC_8H_5)Cr(CO)_3\}_2(dppe)]$ 6. The compound $[Cr(\eta^6\text{-}SC_8H_6)(CO)_3]$ (0.55 g, 2.04 mmol) was dissolved in thf (*ca.* 15 cm^3). The solution was cooled to −40 °C and butyllithium (1.40 cm^3, 2.24 mmol) was added to the stirred solution. Stirring was maintained for 1 h at this temperature during which time the solution changed from orange-red to dark brown. The compound $[Pt(dppe)Cl_2]$ (1.30 g, 2.04 mmol) was gradually added to the cooled reaction mixture, after which stirring was maintained for 30 min. The mixture was heated to room temperature and stirred for 30 min. It was filtered through silica gel, using dichloromethane as eluent. The solvent was removed under reduced pressure and the mixture purified by column chromatography. Two bands were separated using a 1 : 1 mixture of light petroleum (bp 40–60 °C) and dichloromethane as eluent. The first band removed from the column was characterized as $[Cr(\eta^6\text{-}C_8H_6S)(CO)_3]$ (0.30 g, 57%) and the second the target complex $[Pt\{(\eta^6\text{-}C_8H_5S)Cr(CO)_3\}_2(dppe)]$ **6** (0.63 g, 34%) (Found: C, 51.37; H, 3.55. $C_{48}H_{34}Cr_2O_6P_2PtS_2$ requires C, 50.93; H, 3.03%). Mass spectrum: M^+ not observed.

Crystallography

An orange single crystal of approximate size 0.25 × 0.15 × 0.12 mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation (λ = 0.710 73 Å) at 293 K. Important crystallographic parameters are summarized in Table 4.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 27 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 3712 reflections (3388 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz-polarization effects, and empirically for absorption. The 2797 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the triclinic space group $P\bar{1}$.

The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinements and Fourier-difference synthesis. The σ-bound thienyl ligand was disordered over two sites related by a 180° rotation. A model was refined in which atoms C(5), C(7) and C(8) were common to both orientations while the atom pairs S(2a)/C(6a) and S(2b)/C(6b) were refined with common coordinates and thermal parameters but with freely varying occupancy. The orientation shown in Fig. 2 is the dominant (70%) one. The non-hydrogen atoms were refined anisotropically and hydrogens were omitted from the model. The final cycle of least-squares refinement included 218 parameters for 2797 variables and did not shift any parameter by more than 0.0001 times its standard deviation. The final R values were 0.0376 and 0.0405, and the final Fourier-difference map was featureless with no peaks greater than 0.91 e Å^{-3}.

Structure solution used the SHELXTL PLUS program package[50] on a microVax II computer.

CCDC reference number 186/582.

Acknowledgements

We thank Dr. D. Tocher, University College of London, for collecting the crystal data and solving the structure. Also, Mr. E. Palmer for assistance during NMR experiments. We are thankful for financial assistance from the University of Pretoria and the Foundation of Research Development of South Africa.

References

1 Y. M. Terblans and S. Lotz, *J. Chem. Soc., Dalton Trans.*, 1997, 2177.

2 D. W. Stephan, *Coord. Chem. Rev.*, 1989, **95**, 41; W. Beck, B. Niemer and M. Wieser, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923; S. Lotz, P. H. van Rooyen and R. Meyer, *Adv. Organomet. Chem.*, 1995, **37**, 219; J. Forniés and E. Lalinde, *J. Chem. Soc., Dalton Trans.*, 1996, 2587 and refs. therein.

3 R. J. Angelici, *Coord. Chem. Rev.*, 1990, **105**, 61; T. B. Rauchfuss, *Prog. Inorg. Chem.*, 1991, **39**, 259.

4 D. A. Dowden, *Catalysis*, eds. C. Kemball and D. A. Dowden, Specialist Periodic Report, The Chemical Society, London, 1978, vol. 2, p. 1; J. H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts and Applications*, Wiley, New York, 1983.

5 U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; N. L. Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129; M. Sponsler, *Organometallics*, 1995, **14**, 1920; V. W.-W. Yam, V. C.-Y. Lau and K.-K. Cheung, *Organometallics*, 1996, **15**, 1740.

6 M. O. Senge, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1923; N. P. Farrell, *Biochemistry*, 1995, **34**, 15 480.

7 M. Cowie and S. J. Loeb, *Organometallics*, 1985, **4**, 852; S. W. Carr, P. G. Pringle and B. L. J. Shaw, *J. Organomet. Chem.*, 1988, **341**, 543; K. A. Johnson, M. D. Vashon, B. Moasser, B. K. Warmka and W. L. Gladfelter, *Organometallics*, 1995, **14**, 461.

8 U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack and V. V. Burlakov, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1605; U. Rosenthal, S. Pulst, P. Arndt, A. Ohff, A. Tillack, W. Baumann, R. Kempe, A. Tillack and V. V. Burlakov, *Organometallics*, 1995, **14**, 2961.

9 D. Röttger, G. Erker, R. Fröhlich, M. Grehl, S. J. Silverio, I. Hyla-Kryspin and R. Gleiter, *J. Am. Chem. Soc.*, 1995, **117**, 10 503.

10 H. Werner, W. Paul, W. Knaup, J. Wolf, G. Müller and J. Reide, *J. Organomet. Chem.*, 1988, **358**, 95; W. A. Herrmann, B. Reiter and H. Biersack, *J. Organomet. Chem.*, 1975, **97**, 245.

11 G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics*, 1989, **8**, 911; G. Erker, W. Frömberg, R. Mynott, B. Gabor and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 463; J. Forniés, M. A. Gomez-Saso, E. Lalinde, F. Martinez and M. T. Moreno, *Organometallics*, 1992, **11**, 2873; J. Forniés, E. Lalinde, A. Martin and M. T. Moreno, *J. Chem. Soc., Dalton Trans.*, 1994, 135; J. R. Berenguer, J. Forniés, E. Lalinde and A. Martin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2083; J. R. Berenguer, L. Falvello, J. Forniés, E. Lalinde and M. Thomas, *Organometallics*, 1993, **12**, 6; T. Weidmann, V. Weinrich, B. Wagner, C. Robl and W. Beck, *Chem. Ber.*, 1991, **124**, 1363.

12 S. Lotz, M. Schindehutte and P. H. van Rooyen, *Organometallics*, 1992, **11**, 629; P. H. van Rooyen, M. Schindehutte and S. Lotz, *Organometallics*, 1992, **11**, 1104; *Inorg. Chim. Acta*, 1993, **208**, 207; R. Meyer, P. H. van Rooyen, M. Schindehutte and S. Lotz, *Inorg. Chem.*, 1994, **33**, 3605.

13 T. A. Waldbach, P. H. van Rooyen and S. Lotz, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 710; *Organometallics*, 1993, **12**, 4250; T. A. Waldbach, R. van Eldik, P. H. van Rooyen and S. Lotz, *Organometallics*, in the press.

14 T. A. Pecoraro and R. R. Chianelli, *J. Catal.*, 1981, **67**, 430.

15 J. J. Garcia, B. E. Mann, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Am. Chem. Soc.*, 1995, **117**, 2179.

16 T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628; T. J. Giordano, W. M. Butler and P. G. Rasmussen, *Inorg. Chem.*, 1978, **17**, 1917; D. Sandrini, M. Maestri, V. Balzani, L. Chassot and A. von Zelewsky, *J. Am. Chem. Soc.*, 1987, **109**, 7720; M. Nonoyama and S. Kajita, *Transition Met. Chem.*, 1981, **6**, 163.

17 C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1978, 357.

18 J. Klosin, X. Zheng and W. M. Jones, *Organometallics*, 1996, **15**, 3788.

19 M. N. Nefedova, V. N. Setkina and D. N. Kursanov, *J. Organomet. Chem.*, 1983, **244**, C21.

20 J. M. Jenkins, J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1969, 2796.

21 S. Lotz and T. A. Waldbach, unpublished work.

22 S. Kotani, K. Shiina and K. Sonogashira, *J. Organomet. Chem.*, 1992, **429**, 403.

23 V. G. K. Das and L. K. Mun, *J. Organomet. Chem.*, 1987, **334**, 307; V. G. K. Das, L. K. Mun and N. S. Weng, *Main Group Metal Chem.*, 1988, **11**, 251.

24 R. M. Kellogg, *Compr. Heterocycl. Chem.*, 1984, **4**, 771.

25 E. O. Fischer and K. Öfele, *Chem. Ber.*, 1985, **91**, 2395; M. Novi, G. Guanti and C. Dell'Erba, *J. Heterocycl. Chem.*, 1975, **12**, 1055.

26 E. O. Fischer, H. A. Goodwin, C. G. Kreiter, H. D. Simmons, K. Sonogashira and S. B. Wild, *J. Organomet. Chem.*, 1968, **14**, 359.

27 M. A. Bennett, G. B. Robertson, A. Rokicki and W. A. Wickramasinghe, *J. Am. Chem. Soc.*, 1988, **110**, 7098.

28 G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 1246; 1980, 143.

29 G. Bodner and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 360.

30 A. Mangini and T. Taddei, *Inorg. Chim. Acta*, 1968, **2**, 12.

31 E. Lukevits, O. A. Pudova, T. Popelis and N. P. Erchak, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1981, **51**, 102.

32 D. E. Sietz, S.-H. Lee, R. N. Hanson and J. C. Bottaro, *Synth. Commun.*, 1983, **13**, 121; C. van Pham, R. S. Macomber, H. B. Mark, jun. and H. Zimmer, *J. Org. Chem.*, 1984, **49**, 5250.

33 B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135.

34 M. H. Chisholm, H. C. Clark, L. E. Manzer and J. B. Stothers, *Chem. Commun.*, 1971, 1627.

35 D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching and M. Bullpitt, *Aust. J. Chem.*, 1974, **27**, 417.

36 M. H. Chisholm, H. C. Clark, L. E. Manzer and J. E. H. Ward, *J. Am. Chem. Soc.*, 1973, **95**, 8574.

37 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1306.

38 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499.

39 A. L. Reiger, G. B. Carpenter and P. H. Reiger, *Organometallics*, 1993, **12**, 842.

40 M. Sato, E. Mogi and M. Katada, *Organometallics*, 1995, **14**, 4837.

41 D. F. Shriver and M. A. Drezdzon, in *The Manipulation of Air-sensitive Compounds*, 2nd edn., Wiley, New York, 1986.

42 D. D. Perrin, W. L. F. Amarego and D. R. Perrin, in *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, New York, 1980.

43 G. H. Spies and R. J. Angelici, *Organometallics*, 1987, **6**, 1897.

44 W. Wolfsberger and H. Smidbauer, *Synth. Inorg. Metal-Org. Chem.*, 1974, **4**, 149.

45 D. L. Packett, C. M. Jensen, R. L. Cowan, C. E. Strouse and W. C. Trogler, *Inorg. Chem.*, 1985, **24**, 3578.

46 G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1981, **20**, 3607.

47 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

48 C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1978, 1730.

49 M. D. Rausch, G. A. Moser, E. J. Zaiko and A. L. Lipman, jun., *J. Organomet. Chem.*, 1970, **23**, 185.

50 G. M. Sheldrick, SHELXTL PLUS, University of Göttingen, 1986.

Received 2nd April 1997; *Paper* 7/02252B