Metallacyclic Complexes. Part 3.[1] Reactions of Metallathietane 3,3-Dioxide Complexes of Platinum(II) and Palladium(II) with Alkyl Isocyanides; the Single Crystal *X*-Ray Structure of $[\mathrm{Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^t)(PPh_3)]\cdot CHCl_3}$†

William Henderson, Raymond D. W. Kemmitt,* Lesley J. S. Prouse, and David R. Russell
Department of Chemistry, The University, Leicester LE1 7RH

The reactions of the metallathietane 3,3-dioxide complexes $[\mathrm{M\{CHRS(O)_2CHR\}L_2}]$ of platinum(II) and palladium(II) with alkyl isocyanides are dependent on both the mole ratio of isocyanide to metal complex, and on the ring substituent R. Treatment of phenyl-substituted metallathietane 3,3-dioxide complexes with excess of isocyanide results in ligand substitution to afford monosubstituted complexes of the type $[\mathrm{M\{CHRS(O)_2CHPh\}(CNBu^t)L}]$. Similarly, treatment of the benzoyl-substituted complexes $[\mathrm{M\{CH(COPh)S(O)_2CH(COPh)\}L_2}]$ with 1 equivalent of isocyanide also affords monosubstituted complexes $[\mathrm{M\{CH(COPh)S(O)_2CH(COPh)\}(CNR)L}]$ (M = Pt, L = $\mathrm{PPh_3}$, R = $\mathrm{Bu^n}$ or $\mathrm{Bu^t}$; M = Pd, L = $\mathrm{PEt_3}$, R = $\mathrm{Bu^t}$). On treatment of platinathietane 3,3-dioxide complexes containing benzoyl or methoxycarbonyl ring substituents with excess of isocyanide, ring insertion and hydrogen migration occurs to afford the zwitterionic five-membered ring products $[\mathrm{Pt\{CH(COR)S(O)_2\bar{C}(COR)C{=}\overset{+}{N}HR'\}(CNR')L}]$ (L = $\mathrm{PPh_3}$ or $\mathrm{PMe_2Ph}$; R = COPh or $\mathrm{CO_2Me}$; R′ = $\mathrm{Bu^t}$ or $\mathrm{Bu^n}$). Treatment of $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)(CNBu^t)}]$ with 1 equivalent of $\mathrm{Bu^nNC}$, or $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^n)(PPh_3)}]$ with 1 equivalent of $\mathrm{Bu^tNC}$, affords, in both cases, the n-butyl isocyanide-inserted product $[\mathrm{Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^t)(PPh_3)}]$ (**13**), confirmed by a single-crystal *X*-ray diffraction study carried out on (13)$\cdot\mathrm{CHCl_3}$. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with lattice parameters a = 28.337(2), b = 9.625(2), c = 16.507(1) Å, and β = 101.71(5)°. The structure was refined to R 0.0661 (R' 0.0530) for 4 019 reflections having $7 < 2\theta < 54°$ collected at room temperature.

During our investigations of the chemistry of some η^3-oxodimethylenemethane complexes of platinum(II), $[\mathrm{Pt\{\eta^3\text{-}CHRC(O)CHR\}(PPh_3)_2}]$, (**1**), we observed that these complexes reacted with butyl isocyanide to form zwitterionic complexes of the type (**2**).[2] Further studies revealed that these 'insertion' reactions were highly dependent upon the nature of the substituent R on the oxodimethylenemethane ligand since attempts to isolate zwitterionic complexes similar to (**2**) from the reactions of $\mathrm{Bu^tNC}$ with the complexes (**1**; R = H or Ph) were not successful.[3] The availability of a series of metallathietane 3,3-dioxide complexes of platinum(II) and palladium(II) $[\mathrm{Pt\{CHRS(O)_2CHR\}L_2}]$ (**3**)[1,4] led us to investigate the reactions of these complexes with $\mathrm{Bu^tNC}$ in order to establish whether 'insertion' reactions with these systems were also dependent upon the nature of the substituent R in the metallathietane 3,3-dioxide ring system.

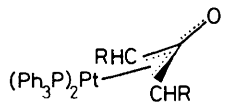
Results and Discussion

The reactions of the phenyl-substituted metallathietane 3,3-dioxide complexes $[\mathrm{M\{CHPhS(O)_2CHPh\}L_2}]$ (**3a**) and (**3b**) with an excess of t-butyl isocyanide in refluxing dichloromethane results in the displacement of one tertiary phosphine or phosphite ligand to afford the monosubstituted metallathietane 3,3-dioxide complexes (**4a**) and (**4b**) respectively there being no evidence for insertion of the isocyanide into the four-membered metallacyclic rings. Complexes (**4a**) and (**4b**) show the expected i.r. spectroscopic features for such monosubstituted complexes, with a single, intense terminal isocyanide band being observed at 2 198 $\mathrm{cm^{-1}}$ for (**4a**) and 2 185 $\mathrm{cm^{-1}}$ for (**4b**). Previous studies[4] on $[\mathrm{Pt\{CHPhS(O)_2CHPh\}(AsPh_3)_2}]$ have established the presence of a slightly puckered platinathietane 3,3-dioxide ring with one of the phenyl groups and one S=O group in pseudo-axial environments. A similar conformation is probably present in the monosubstituted derivatives (**4a**) and (**4b**). The ^{1}H n.m.r. spectra of (**4a**) and (**4b**), measured at room temperature, showed the expected features for either a static or rapidly inverting ring with inequivalent metallathietane 3,3-dioxide ring proton signals displaying ^3J(PH) coupling. However, as for the related complexes $[\mathrm{Pt(CHRCOCHR)(CNBu^t)L}]$ (R = $\mathrm{CO_2Me}$, L = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$),[2] there were no significant changes observable in the ^{1}H n.m.r. spectra of (**4a**) and (**4b**) between 25 and −90 °C.

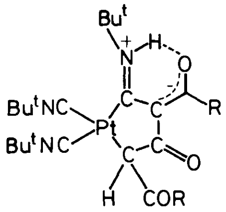
Treatment of the benzoyl-substituted platinathietane 3,3-dioxide (**3c**) with 1 mol equivalent of either t-butyl isocyanide or n-butyl isocyanide, or the palladium complex (**3d**) with 1 mol equivalent of t-butyl isocyanide in dichloromethane, affords the air-stable monosubstituted metallathietane 3,3-dioxide complexes $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNR)L}]$ [M = Pt, L = $\mathrm{PPh_3}$, R = $\mathrm{Bu^t}$ (**5a**) or $\mathrm{Bu^n}$ (**5b**); M = Pd, L = $\mathrm{PEt_3}$, R = $\mathrm{Bu^t}$ (**5c**)] in high yield. The i.r. and n.m.r. (^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H}) spectroscopic properties are characteristic for monoisocyanide metallathietane 3,3-dioxide complexes. Thus,

---

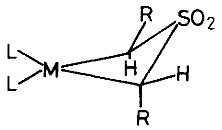
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



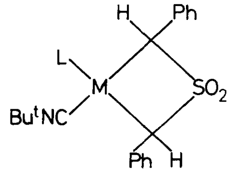
(1) R = Me or OMe



(2) R = Me or OMe

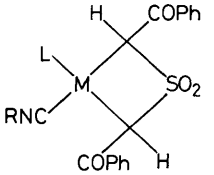


	M	R	L
(3a)	Pt	Ph	$P(OMe)_3$
(3b)	Pd	Ph	PMe_3
(3c)	Pt	COPh	PPh_3
(3d)	Pd	COPh	PEt_3
(3e)	Pt	COPh	PMe_2Ph
(3f)	Pt	CO_2Me	PPh_3

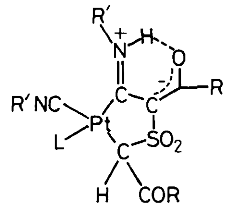


(4a) M = Pt, L = $P(OMe)_3$

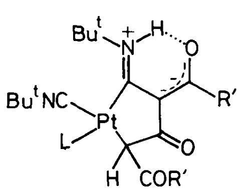
(4b) M = Pd, L = PMe_3



	M	L	R
(5a)	Pt	PPh_3	Bu^t
(5b)	Pt	PPh_3	Bu^n
(5c)	Pd	PEt_3	Bu^t



	L	R	R′
(6a)	PPh_3	Ph	Bu^t
(6b)	PMe_2Ph	Ph	Bu^t
(6c)	PPh_3	Ph	Bu^n
(6d)	PPh_3	OMe	Bu^t

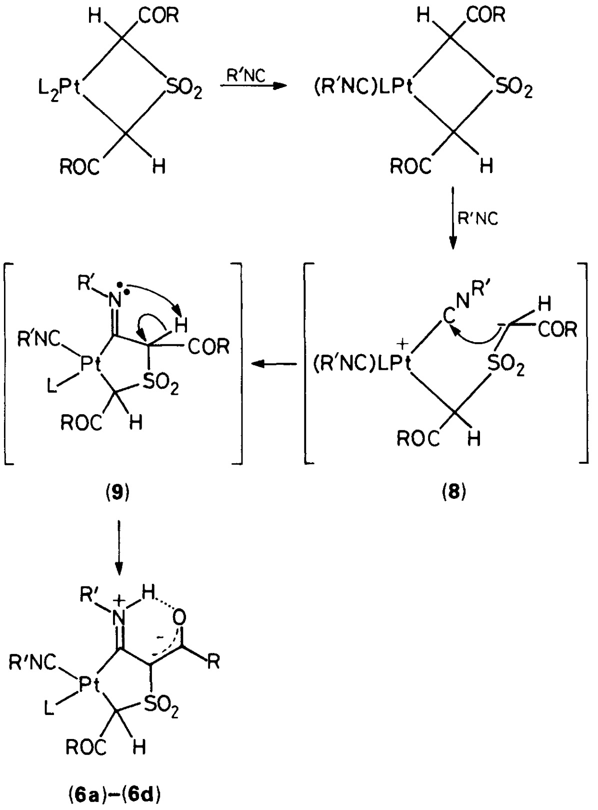


(7) R′ = Me or OMe
L = Bu^{t}NC or PPh_3

the ^1H and ^{13}C-{^1H} n.m.r. spectra show the presence of two inequivalent Pt–CH groups, with the one *trans* to the phosphine ligand displaying the larger $^2J(PC)$ and $^3J(PH)$ couplings. One of the carbonyl groups in the ^{13}C-{^1H} n.m.r. spectrum of (**5a**) shows coupling to both the phosphorus ligand [$^3J(PC)$ 3.9 Hz] and the platinum-195 nucleus [$^2J(PtC)$ 44.5 Hz], whereas the other carbonyl group, presumably *cis* to the phosphine ligand, shows coupling to platinum-195 only, with $^2J(PtC)$ *ca.* 37 Hz. The behaviour of these benzoyl-substituted metallathietane 3,3-dioxide complexes is very similar to that displayed by ketone- or ester-substituted oxodimethylenemethane complexes, of platinum and palladium, which also undergo simple ligand substitution with 1 equivalent of isocyanide.[2] The behaviour of these benzoyl- or methoxycarbonyl-substituted metallathietane 3,3-dioxide complexes with an excess of isocyanide also mimics the chemistry displayed by the oxodimethylenemethane complexes.[2] Thus, treatment of the platinathietane 3,3-dioxide complexes (**3c**), (**3e**), and (**3f**) with an excess of either t-butyl or n-butyl isocyanide in refluxing dichloromethane resulted in ring insertion to afford white to pale yellow crystalline complexes formulated as the zwitterionic five-membered ring products $[\mathrm{Pt\{CH(COR)S(O)_2C(COR)C{=}\overset{+}{N}HR'\}(CNR')L}]$ [L = PPh_3, R = Ph, R′ = Bu^t (**6a**), L = PMe_2Ph, R = Ph, R′ = Bu^t (**6b**), L = PPh_3, R = Ph, R′ = Bu^n (**6c**), or L = PPh_3, R = OMe, R′ = Bu^t (**6d**)] on the basis of their i.r. and n.m.r. spectroscopic properties, and a single-crystal *X*-ray diffraction study on a mixed isocyanide analogue, which is described later.

The spectroscopic properties of complexes (**6a**)—(**6d**) are almost identical with those of the related ketone complexes (**7**) containing a phosphine ligand.[2] Thus, the ^1H n.m.r. spectra of (**6a**)—(**6d**) display a characteristic broad low-field signal at > δ 10 due to the acidic iminium proton, which is readily exchanged on shaking with alkaline [$^2H_2$]water. This NH proton signal shows a large coupling of the *trans* phosphorus-31 nucleus to give a doublet, with values of $^4J(PH)$ being around 14.4 Hz. Satellite features due to coupling to platinum-195 are also observed, with $^3J(PtH)$ in the range 78—95 Hz. Although this acidic proton is far removed from the phosphorus and platinum nuclei, this long-range coupling is similar to the large couplings observed between *trans* substituents in olefins. For the n-butyl isocyanide complex (**6c**), the NH proton shows an additional coupling to the α-CH_2 protons of the inserted n-butyl group, to give a broad, complex multiplet, but no phosphorus or proton coupling could be resolved. The Pt–CH protons for complexes (**6a**)—(**6d**) appear in the range δ 3.8—5.0, showing coupling to both the *cis* phosphine ligand, with $^3J(PH)$ values in the range 10.7—11.2 Hz, and to the platinum-195 nucleus, with $^2J(PtH)$ in the range 75.0—84.0 Hz. These values are similar to those of the parent platinathietane 3,3-dioxide complexes, which we have described previously,[1] and to those of the monosubstituted complexes. Two sets of t-butyl or n-butyl resonances are observed in the ^1H and ^{13}C-{^1H} n.m.r. spectra of (**6a**)—(**6d**) due to the two non-equivalent (co-ordinated and inserted) isocyanide moieties. By comparison of the ^1H n.m.r. chemical shifts of the two t-butyl resonances of (**6a**) with that of the co-ordinated t-butyl isocyanide in the monosubstituted complex (**5a**), the lower-frequency t-butyl resonance of (**6a**) is assigned to the co-ordinated ligand.

The ^{31}P-{^1H} n.m.r. spectra of complexes (**6a**)—(**6d**) show a single resonance with a relatively small coupling to platinum-195, as compared to the parent platinathietane 3,3-dioxide complexes. Thus, values of $^1J(PtP)$ for (**6a**)—(**6d**) lie in the range 1 919—1 997 Hz, whereas the values for the parent platinathietane 3,3-dioxide complexes lie in the range 2 734—2 817 Hz.



Scheme 1.

This suggests that the phosphine ligand in (**6a**)—(**6d**) is *trans* to a C=$\overset{+}{\text{N}}$HR fragment, having high *trans* influence.

The ^{13}C-{^{1}H} n.m.r. spectra of complexes (**6a**)—(**6d**) are also consistent with their formulation as five-membered ring-insertion products. The Pt–CH ring carbons of complexes (**6a**) and (**6b**) exhibit a large ^1J(PtC) coupling of 614.0 and 569.8 Hz respectively, and the presence of a small phosphorus coupling of around 3.8 Hz is consistent with the assignment of these carbons as *cis* to the co-ordinated phosphine ligand. Furthermore, the C=N carbon appears as a weak resonance at δ 186.7 and 189.45 p.p.m. for (**6a**) and (**6b**) respectively, showing very large couplings to both the phosphorus-31 and platinum-195 nuclei. Thus, for example, the values of ^2J(PC) and ^1J(PtC) for the C=N carbon of (**6b**) are 114.5 and 798.1 Hz respectively, consistent with the assignment of an inserted isocyanide moiety *trans* to the co-ordinated phosphine ligand. The carbonyl resonances of (**6a**) and (**6b**) are assigned by their smaller values of J(PC) and J(PtC). Thus the Pt-CH(COPh) carbonyl group of (**6b**) appears at δ 194.92 p.p.m., showing coupling to platinum-195 of 34.7 Hz, these values being similar to those of the parent platinathietane 3,3-dioxide complex (**3e**) [δ 197.23 p.p.m., ^2J(PtC) 32.0 Hz].[1] The $\bar{\text{C}}$–COPh carbonyl appears as a peak at around δ 189 p.p.m. showing coupling to both platinum-195 and phosphorus-31 nuclei. Thus, for example, for complex (**6b**) the values of ^3J(PtC) and ^4J(PC) for the $\bar{\text{C}}$–COPh carbonyl are 62.3 and 1.9 Hz respectively, these relatively large long-range couplings being consistent with the assignment of this group *trans* to the co-ordinated phosphine ligand. The 'carbanionic' ring carbon appears as a weak resonance at δ 120.8 p.p.m. for (**6a**) and 120.3 p.p.m. for (**6b**). A coupling of this carbon to platinum-195 of around 30 Hz was discernible only for (**6b**), and the absence of an attached proton on this carbon is demonstrated by the presence of a single peak in the proton-coupled ^{13}C n.m.r. spectrum of complex (**6b**).

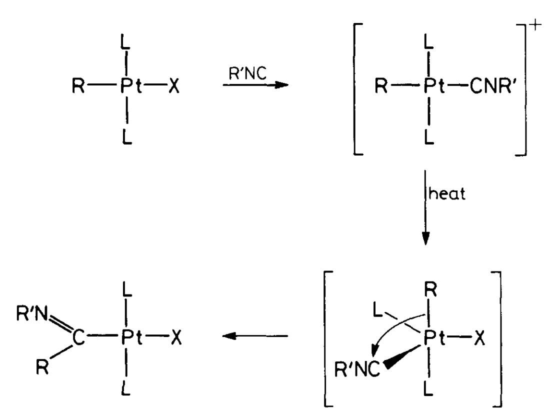
The i.r. spectra of complexes (**6a**)—(**6d**) exhibit a number of weak, broad bands above 3 000 cm^{-1}, assigned to, or at least in part to, the $\overset{+}{\text{N}}$H group, together with an intense band due to the co-ordinated isocyanide ligand in the range 2 084—2 260 cm^{-1}. The somewhat broad band in the range 1 660—1 686 cm^{-1} is assigned to the benzoyl or methoxycarbonyl groups, and the C=N stretch is tentatively assigned as the strong band in the range 1 560—1 583 cm^{-1}.[2] Finally, the sulphone group displays its characteristically intense stretching frequencies in the ranges 1 124—1 140 and 1 297—1 308 cm^{-1}.[5]

In contrast to the above reactions with platinum, the reactions of benzoyl-substituted palladathietane 3,3-dioxide complexes with an excess of Bu^{t}NC afforded bright yellow oils, from which no pure complexes could be isolated.

Hence, as described in this paper, and previously,[1] the two 'series' of platinathietane 3,3-dioxide complexes react differently towards an excess of alkyl isocyanide with phenyl-substituted complexes undergoing simple ligand substitution, and benzoyl- and methoxycarbonyl-substituted complexes undergoing a ring-insertion reaction.

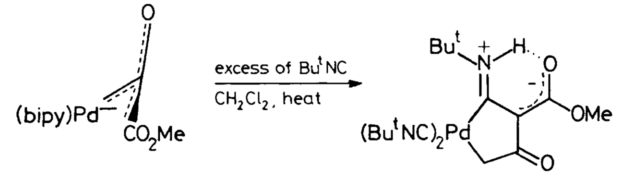
A possible mechanism for the insertion of an alkyl isocyanide into the platinathietane 3,3-dioxide ring system is outlined in Scheme 1. The generation of a monosubstituted metallathietane 3,3-dioxide complex is followed by 'insertion' of a second molecule of isocyanide into a platinum–carbon bond. The differing reactivities of phenyl- and benzoyl-substituted complexes indicate that the presence of electron-withdrawing substituents on the platinathietane 3,3-dioxide ring is a prerequisite for the 'insertion' step. Although the mechanism of this insertion step is not strictly known, the pathway illustrated in Scheme 1 provides a very attractive route to the generation of the ring systems (**6a**)— (**6d**). Thus, platinum–carbon bond cleavage, affording an intermediate zwitterionic complex (**8**), followed by attack of the displaced carbanionic centre of (**8**) upon a co-ordinated isocyanide molecule would generate the isocyanide-inserted ring system (**9**). Finally, an inter- or intra-molecular proton shift from carbon to nitrogen would amount for the formation of the observed zwitterionic complexes (**6a**)—(**6d**). The generation of the zwitterionic intermediate (**8**) is most readily accomplished when the platinathietane 3,3-dioxide ring substituent is an electron-withdrawing group, *viz.* COPh or CO$_2$Me, since the carbanionic centre which is generated in (**8**) will be stabilised by the benzoyl or methoxycarbonyl substituent. Alternatively, however, a concerted migration of a CH(COR) group onto a co-ordinated isocyanide molecule, again promoted by the presence of strongly electron-withdrawing substituents, would also result in the generation of the five-membered ring system (**9**). The actual insertion process may, in practice, be somewhere in between these two limiting descriptions.

It is noteworthy that the reactions of a number of triphenylphosphineplatinum *cis*-dialkyl or -diaryl complexes with isocyanides typically result in substitution only. Thus, treatment of the dialkyl or diaryl complexes *cis*-[PtR$_2$(PPh$_3$)$_2$] (R = Me or Ph) with methyl or *p*-chlorophenyl isocyanides affords the substitution products *cis*-[PtR$_2$(CNR′)(PPh$_3$)] (R′ = Me or *p*-C$_6$H$_4$Cl),[6] and the reactions of [PtR$_2$(PMePh$_2$)$_2$] (R = Me or Ph) with *p*-chlorophenyl isocyanide and of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with *p*-methoxyphenyl isocyanide also afford analogous monosubstitution products.[6,7] However, the presence of a smaller and more basic phosphine, such as triethylphosphine, does result in isocyanide insertion, *e.g.* in the reactions of *cis*-[PtR$_2$(PEt$_3$)$_2$] (R = Me or Ph) with methyl or *p*-chlorophenyl isocyanides, which afford *cis*- or *trans*-[PtR(CR=NR′)(PEt$_3$)$_2$] (R′ = Me or *p*-C$_6$H$_4$Cl).[6] Treatment of the platinacyclobutane complex $[\overline{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2)}(\text{bipy})]$ (bipy = 2,2′-bipyridine) with Bu^{t}NC also results in ligand substitution only, to afford $[\overline{\text{Pt}(\text{CH}_2\text{CH}_2\text{C}}\text{H}_2)(\text{CNBu}^t)_2]$.[8]



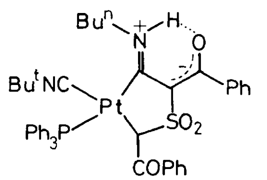
(10)

Scheme 2.



(11) (12)

Scheme 3.



(13)

In contrast to the reactions of dialkyl- or diaryl-platinum complexes with isocyanides, the reactions of a range of complexes of the type *trans*-$[\mathrm{PtR(X)L_2}]$ (X = halide, R = alkyl or aryl, L = tertiary phosphine) with a number of isocyanides R'NC initially affords adducts of the form $[\mathrm{PtR(CNR')L_2}]^+\mathrm{X}^-$, which undergo a migratory insertion of isocyanide on heating, to give the iminoacyl complexes *trans*-$[\mathrm{PtX(CN{=}NR')L_2}]$.[6,9–12] The proposed mechanism for this insertion reaction is illustrated in Scheme 2,[9,10] and bears a resemblance to the mechanism proposed for isocyanide insertion into metallathietane 3,3-dioxide rings (Scheme 1), in that the initial step involves displacement of a ligand from platinum by an isocyanide, forming a cationic platinum centre. Attack of the halide ion at the platinum subsequently effects the concerted migration of the alkyl or aryl residue R to the co-ordinated isocyanide of the intermediate (**10**), to generate the observed iminoacyl complex,[10] and a similar concerted alkyl-migration process has been proposed for the insertion of isocyanides into the platinum–carbon bonds of *cis*-$[\mathrm{PtR_2(PEt_3)_2}]$ (R = Me or Ph).[6] We also note that the reactions of isocyanides with *trans*-$[\mathrm{PdCl(CH_2COMe)(PPh_3)_2}]$ yield the 3-oxobut-1-enyl complexes *trans*-$[\mathrm{PdCl\{C(CNR){=}CHCOMe\}(PPh_3)_2}]$ (R = Me or *p*-$\mathrm{C_6H_4OMe}$).[13]

From the observations above, the presence of electron-withdrawing substituents on the α-carbon atoms of platinathietane 3,3-dioxide rings would appear to be a prerequisite for isocyanide insertion, with these electron-withdrawing groups stabilising the intermediate species in the insertion step. Consistent with this, a number of platinaoxodimethylene-withdrawing alkoxycarbonyl or acetyl substituents also readily undergo insertion reactions with Bu^{t}NC to afford complexes (**7**), which are analogous to the sulphone complexes described in this paper.[2] In order further to test the necessity of electron-withdrawing substituents for isocyanide insertion, the monosubstituted palladaoxodimethylenemethane complex (**11**) was treated with an excess of Bu^{t}NC in refluxing dichloromethane. This resulted in highly selective insertion into the Pd–$\mathrm{CH(CO_2Me)}$ bond only, to afford a high yield of the five-membered ring product (**12**), Scheme 3. No evidence of any complexes formed by insertion of isocyanide into the Pd–$\mathrm{CH_2}$ bond was observed.

Complex (**12**) was characterised by its n.m.r. spectroscopic properties, which showed the characteristic features for the five-membered zwitterionic ring system.[2] Thus, the NH proton appears as a characteristically broad peak at δ 10.68, of relative intensity one, and the Pd–$\mathrm{CH_2}$ protons appear as a singlet of relative intensity two, at δ 2.75, indicating that insertion into the Pd–$\mathrm{CH(CO_2Me)}$ bond had occurred. The proton-coupled ^{13}C n.m.r. spectrum of (**12**) is particularly diagnostic, and displays the expected triplet for the Pd–$\mathrm{CH_2}$ group, showing ^1J(CH) 137.1 Hz. The C=N carbon appeared as a doublet in the ^{13}C n.m.r. spectrum due to coupling to the NH proton, with ^2J(CH) 5.3 Hz. Complex (**12**) was air-sensitive in solution, and decomposed over 12 h to give a dark brown oil from which no pure complexes could be identified.

In an attempt to establish further details of the insertion mechanism into these platinathietane 3,3-dioxide ring systems, and into the oxodimethylenemethane complexes, the monosubstituted platinathietane 3,3-dioxide complexes (**5a**) and (**5b**) containing t-butyl isocyanide and n-butyl isocyanide ligands have been treated with 1 equivalent of the alternative isocyanide. Treatment of the monosubstituted platinathietane 3,3-dioxide complex (**5a**) with 1 equivalent of Bu^{n}NC or (**5b**) with 1 equivalent of Bu^{t}NC in refluxing dichloromethane afforded, in both cases, the zwitterionic ring-inserted product (**13**). The ^{1}H n.m.r. spectrum of (**13**) is consistent with the presence of a co-ordinated t-butyl isocyanide ligand, together with an inserted $\mathrm{C{=}\overset{+}{N}HBu^n}$ moiety. Thus, the NH proton appears as a complex multiplet, as observed for the other inserted n-butyl isocyanide complex (**6c**) due to coupling to platinum-195, phosphorus-31, and the α-$\mathrm{CH_2}$ protons of the n-butyl group. A comparison of the chemical shift for the t-butyl resonance of (**13**) with the t-butyl resonances of the monosubstituted and ring-inserted complexes, (**5a**) and (**6a**) respectively, confirms the presence of a co-ordinated, as opposed to an inserted, t-butyl isocyanide ligand. Why only insertion of Bu^{n}NC occurs is uncertain. Following the mechanism proposed in Scheme 1 for the isocyanide insertion in platinathietane 3,3-dioxide complexes, preferential attack of the carbanionic centre on the co-ordinated n-butyl isocyanide ligand, in an intermediate of the type (**8**), would account for the selective formation of (**13**). The isocyanide carbon of the n-butyl isocyanide ligand would be expected to be more susceptible to nucleophilic attack than that of a t-butyl isocyanide ligand, as a result of steric and electronic effects.

It is not possible to rule out the selective formation of a zwitterionic intermediate of the type (**8**) (Scheme 1) having the carbanionic alkyl ligand *trans* to the Bu^{t}NC, a geometry which would prohibit 'insertion' of Bu^{t}NC. The possibility of substitution of one isocyanide for another in the monosubstituted complexes prior to insertion of Bu^{n}NC also cannot be discounted.

The formulation of the isocyanide insertion products was confirmed by a single-crystal *X*-ray diffraction study carried out on the mixed isocyanide complex (**13**)·$\mathrm{CHCl_3}$. The molecular

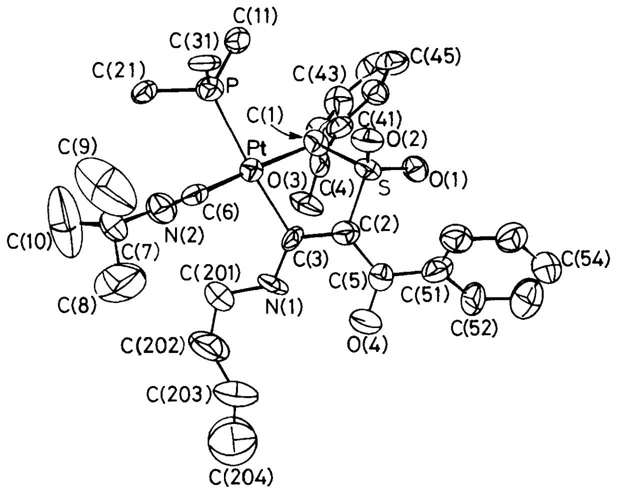


Figure. Molecular structure of $[\mathrm{Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^t)(PPh_3)}]$ (**13**) with triphenylphosphine carbon atoms other than those bonded to phosphorus, and all hydrogen atoms, omitted

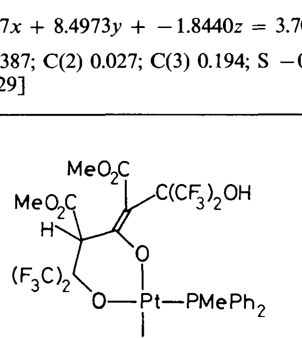
Table 1. Selected bond lengths (Å) and angles (°) for the complex $[\mathrm{P\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^t)(PPh_3)}]$ (**13**) $\cdot\mathrm{CHCl_3}$

Pt–P	2.325(4)	C(2)–C(5)	1.446(19)
Pt–C(6)	1.908(11)	C(5)–O(4)	1.246(17)
Pt–C(1)	2.080(10)	C(1)–C(4)	1.547(17)
Pt–C(3)	2.060(13)	C(4)–O(3)	1.218(17)
C(6)–N(2)	1.197(15)	N(1)–C(201)	1.510(20)
C(3)–N(1)	1.333(17)	C(201)–C(202)	1.331(27)
C(2)–C(3)	1.396(16)	C(202)–C(203)	1.50(4)
C(1)–S	1.765(13)	C(203)–C(204)	1.32(4)
C(2)–S	1.741(13)	C(7)–C(8)	1.45(3)
S–O(1)	1.454(8)	C(7)–C(9)	1.44(4)
S–O(2)	1.454(11)	C(7)–C(10)	1.56(4)
P–Pt–C(6)	87.7(4)	C(3)–C(2)–C(5)	124.2(12)
P–Pt–C(1)	95.1(4)	Pt–C(3)–C(2)	116.4(10)
C(1)–Pt–C(3)	82.3(5)	O(1)–S–O(2)	115.5(5)
C(3)–Pt–C(6)	94.5(5)	C(2)–C(5)–O(4)	121.1(12)
C(6)–N(2)–C(7)	175.7(16)	O(4)–C(5)–C(51)	115.8(12)
Pt–C(1)–S	103.5(5)	C(1)–C(4)–O(3)	123.4(11)
C(1)–S–C(2)	100.5(6)	C(3)–N(1)–C(201)	125.0(12)
S–C(2)–C(3)	113.4(10)	N(1)–C(201)–C(202)	111.8(18)
S–C(2)–C(5)	122.1(9)		

Table 2. Equation of least-squares plane in the form $Ax + By + Cz = D$, for complex (**13**), where x, y, and z are fractional co-ordinates, through Pt, C(1), C(2), C(3), and S with deviations (Å) of relevant atoms given in square brackets

$$13.3007x + 8.4973y + -1.8440z = 3.7012$$

[Pt −0.297; C(1) 0.387; C(2) 0.027; C(3) 0.194; S −0.310; C(5) 0.261; O(4) 0.746; N(1) 0.729]



(**14**)

structure is illustrated in the Figure, together with the crystallographic numbering system, and important bond lengths and angles are given in Table 1.

The molecular structure consists of a five-membered ring containing a $\mathrm{Pt(CNBu^t)(PPh_3)}$ moiety. The co-ordination about the platinum atom is effectively square planar, with a small twist angle of 8.78(53)° between the P–Pt–C(6) and C(1)–Pt–C(3) planes. Overall, the geometry of complex (**13**) bears a very strong resemblance to that of the ketone analogue (**7**; L = $\mathrm{Bu^tNC}$, R′ = OMe), which was prepared *via* the reaction of $[\mathrm{Pt\{\eta^3\text{-}CH(CO_2Me)C(O)CH(CO_2Me)\}(PPh_3)_2}]$ with 3 mol equivalents of $\mathrm{Bu^tNC}$.[2] Examination of the geometry around C(2) shows this carbon to be sp^2 hybridised, effectively lying in the plane formed by Pt, C(1), C(2), C(3), and S, deviating by only 0.027 Å from the least-squares plane through these atoms (Table 2). The C(2)–C(5) and C(5)–O(4) bonds are respectively shorter and longer than C(1)–C(4) and C(4)–O(3), suggesting that there is a considerable delocalisation of the negative charge which is formally on C(2). The C(2)–C(3) bond appears normal [1.396(16) Å], but the C(2)–S bond is slightly shorter than the C(1)–S bond, suggesting a little stabilisation of the negative charge by the sulphone group. The short C(3)–N(1) bond of 1.333(17) Å is typical of a carbon–nitrogen double bond.[14] It was not possible to locate the hydrogen atom on N(1) in the *X*-ray study, however this hydrogen would be expected to be directed towards the oxygen atom O(4), to form a weak, intramolecular hydrogen bond, as observed in the ketone analogue (**5**; L = $\mathrm{Bu^tNC}$, R′ = OMe), where the iminium proton was located in the *X*-ray study. The Pt–CH hydrogen atom could also not be located. It is worth noting that the C(201)–C(202) and C(203)–C(204) bond distances are somewhat shorter, at 1.331(27) and 1.32(4) Å, than the C(202)–C(203) bond distance of 1.50(4) Å. This may be due to the large thermal parameters associated with these carbons, this being known to effect an artificial shortening of bond distances.[15]

Pyrolysis studies on either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide at 250 °C have been shown to result in the elimination of sulphur dioxide from the strained four-membered ring system, yielding in each case an equilibrium mixture of *cis*- and *trans*-1,2-diphenylcyclopropane.[16] However, heating the platinathietane 3,3-dioxide complex (**3c**) to 250 °C did not effect the elimination of sulphur dioxide, and only unreacted (**3c**) was isolated. This observation is consistent with both the reduced ring strain in (**3c**) (as a result of substitution of carbon by a substantially larger platinum atom), and with the presence of relatively shorter (and therefore stronger) carbon–sulphur bonds in the metallacycle.[1]

The similarity in the behaviour of benzoyl- and methoxycarbonyl-substituted platinathietane 3,3-dioxide and platinaoxodimethylenemethane complexes towards isocyanide insertion[2] led to an investigation of the reactivity of the former towards hexafluoroacetone. The reaction of the oxodimethylenemethane complex $[\mathrm{Pt\{\eta^3\text{-}CH(CO_2Me)C(O)CH(CO_2Me)\}(PPh_3)_2}]$ with hexafluoroacetone has been shown to result in ring expansion to afford the oxygen-bonded complex (**14**).[17] No ring opening of a platinathietane 3,3-dioxide ring was observed, however, on treating the complex (**3c**) with an excess of hexafluoroacetone, with only the solvated product (**3c**)$\cdot\mathrm{C(CF_3)_2(OH)_2}$ being isolated in high yield.

Treatment of complex (**3c**) with 1 equivalent of (phenylsulphonyl)acetic acid in dichloromethane at room temperature resulted in the recovery of unreacted starting material (**3c**), according to $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectroscopy. On refluxing the mixture for 30 min, reaction occurred, resulting in the formation of a 1:1 mixture of unreacted (**3c**) and the bis(carboxylato) complex *cis*-$[\mathrm{Pt\{OC(O)CH_2SO_2Ph\}_2(PPh_3)_2}]$ (**15**). Complex (**15**) was identified in the mixture by comparison of its $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum with that of an authentic sample of (**15**) prepared from *cis*-$[PtCl_2(PPh_3)_2]$, (phenylsulphonyl)acetic acid, and silver(I) oxide in refluxing dichloromethane. The formation of this mixture indicates that cleavage of the second platinum–carbon bond is much more rapid than the initial cleavage of a metallacyclic platinum–carbon bond.

Experimental

Melting points were measured in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded in $[^2H_1]$chloroform on a Varian EM390 spectrometer at 90 MHz, on a Bruker AM300 spectrometer at 300.13 MHz, and on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz, with $SiMe_4$ (δ 0.0) as internal reference, positive values being to high frequency (low field). Carbon-13, hydrogen-1 decoupled n.m.r. spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz and on a Bruker Spectrospin WH400 spectrometer at 100.62 MHz with $SiMe_4$ (δ 0.0) as internal reference, in $[^2H_1]$chloroform. Phosphorus-31, hydrogen-1 decoupled n.m.r. spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz, with $[P(OH)_4]^+$ in $[^2H_2]$water (δ 0.0 p.p.m.) as external reference,[18] and on a Bruker Spectrospin WH400 spectrometer at 162 MHz with 85% H_3PO_4 as external reference. The fluorine-19, hydrogen-1 decoupled n.m.r. spectrum was recorded in $[^2H_1]$chloroform on a JEOL JNM-PS100 spectrometer, at 94.1 MHz, relative to external trichlorofluoromethane.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction of b.p. 40—60 °C. The acid $PhSO_2CH_2CO_2H$ was prepared from $PhSCH_2CO_2H$ by the literature procedure.[19] The metallathietane 3,3-dioxide complexes[1,4] and $[PtCl_2(cod)]$[20] (cod = cyclo-octa-1,5-diene) were prepared as described in the literature. The complex $[Pd\{\eta^3\text{-}CH_2C(O)CH(CO_2Me)\}(bipy)]$ (**11**) was prepared *via* the literature procedure for the preparation of the ethyl ester analogue,[21] and yielded comparable ^1H n.m.r. spectroscopic properties.

Reactions of Phenyl-substituted Metallathietane 3,3-*Dioxide Complexes with Alkyl Isocyanides*.—(*i*) *Preparation of* $[Pt\{CHPhS(O)_2CHPh\}(CNBu^t)\{P(OMe)_3\}]$(**4a**). A solution of $[Pt\{CHPhS(O)_2CHPh\}\{P(OMe)_3\}_2]$ (0.10 g, 1.145 mmol) in dichloromethane (20 cm^3) with t-butyl isocyanide (0.1 g, 1.2 mmol) was stirred for 1 h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane–light petroleum to afford white *microcrystals* of complex (**4a**) (0.072 g, 77%) (Found: C, 41.2; H, 4.9; N, 2.1. $C_{22}H_{30}NO_5PPtS$ requires C, 40.9; H, 4.7; N, 2.2%), m.p. 180—183 °C; ν(CN) at 2 198s; ν(SO_2) at 1 110vs and 1 271w cm^{-1}. N.m.r. spectra: ^1H (400 MHz), δ 7.47—7.03 (m, 10 H, Ph), 4.40 [d, 1 H, Pt–CH, ^3J(PH) *trans* 12.2, ^2J(PtH) 69.9], 4.35 [d, 1 H, Pt–CH, ^3J(PH) *cis* 8.34, ^2J(PtH) 77.8], 3.42 [d, 9 H, $P(OMe)_3$, ^3J(PH) 12.35], and 1.13 (s, 9 H, Bu^t); $^{31}P\text{-}\{^1H\}$ (24 MHz), δ 118.19 p.p.m. [s, ^1J(PtP) 4 732 Hz].

(*ii*) *Preparation of* $[Pd\{CHPhS(O)_2CHPh\}(CNBu^t)(PMe_3)]$ (**4b**). A solution of $[Pd\{CHPhS(O)_2CHPh\}(PMe_3)_2]$ (0.10 g, 0.20 mmol) in dichloromethane (20 cm^3) with Bu^tNC (0.1 g, 1.2 mmol) was refluxed for 12 h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane–light petroleum to give white *microcrystals* of complex (**4b**) (0.076 g, 75%) (Found: C, 52.0; H, 5.9; N, 2.9. $C_{22}H_{30}NO_2PPdS$ requires C, 51.8; H, 5.9; N, 2.8%), m.p. 174—178 °C (decomp.); ν(CN) at 2 185s; ν(SO_2) at 1 107vs and 1 270m cm^{-1}. N.m.r. spectra: ^1H (400 MHz), δ 7.42—6.99 (m, 10 H, Ph), 3.95 [d, 1 H, Pd–CH, ^3J(PH) 8.59], 3.63 [d, 1 H, Pd–CH, ^3J(PH) 8.07], 1.17 (s, 9 H, Bu^t), and 1.03 [d, 9 H, PMe_3, ^2J(PH) 8.59 Hz]; $^{31}P\text{-}\{^1H\}$ (162 MHz, $[^2H_1]$chloroform), δ −20.0 p.p.m. (s).

Reactions of Benzoyl- and Methoxycarbonyl-substituted Metallathietane 3,3-*Dioxide Complexes with Alkyl Isocyanides*.—(*a*) *With* 1 *equivalent of isocyanide*. (*i*) *Preparation of* $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^t)(PPh_3)]$ (**5a**). t-Butyl isocyanide (0.015 g, 0.181 mmol) in dichloromethane (*ca.* 10 cm^3) was added dropwise to a stirred solution of $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]$ (**3c**)·CH_2Cl_2·0.5H_2O (0.20 g, 0.18 mmol) in dichloromethane (20 cm^3), and the mixture refluxed for 30 min. Evaporation to dryness under reduced pressure afforded a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 2 cm^3) followed by addition of light petroleum (50 cm^3) afforded white *microcrystals* of complex (**5a**) (0.133 g, 88%) (Found: C, 55.1; H, 4.5; N, 1.5. $C_{39}H_{36}NO_4PPtS$ requires C, 55.7; H, 4.3; N, 1.7%), m.p. 114—117 °C; ν(CN) at 2 192vs; ν(SO_2) at 1 121vs and 1 302s cm^{-1}. N.m.r. spectra: ^1H (300 MHz), δ 8.30—7.09 (m, 30 H, Ph), 5.36 [d, 1 H, Pt–CH, ^3J(PH) *trans* 9.32, ^2J(PtH) 72.0], 4.80 [d, 1 H, Pt–CH, ^3J(PH) *cis* 5.76, ^2J(PtH) 66.3], and 0.69 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 196.11 [s, CO, ^2J(PtC) *ca.* 37], 193.41 [d, CO, ^2J(PtC) 44.5, ^3J(PC) 3.9], 58.12 (s, C, Bu^t), 52.91 [d, Pt–CH, ^2J(PC) *cis* 3.01, ^1J(PtC) 471.7], 52.36 [d, Pt–CH, ^2J(PC) *trans* 65.06, ^1J(PtC) 324.9], and 28.85 p.p.m. (s, Bu^t); $^{31}P\text{-}\{^1H\}$ (24 MHz), δ 12.71 p.p.m. [s, ^1J(PtP) 2 832 Hz].

(*ii*) *Preparation of* $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^n)(PPh_3)]$ (**5b**). n-Butyl isocyanide (0.015 g, 0.181 mmol) in dichloromethane (*ca.* 10 cm^3) was added dropwise to a stirred solution of complex (**3c**)·CH_2Cl_2·0.5H_2O (0.20 g, 0.18 mmol) in dichloromethane (20 cm^3), and the solution evaporated to dryness under reduced pressure to afford a pale yellow oil, which was shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy to be a 1:1 mixture of the required complex and liberated triphenylphosphine. Dissolution of the oil in dichloromethane (0.5 cm^3) followed by addition of light petroleum afforded white *microcrystals* of complex (**5b**) (0.126 g, 85%). N.m.r. spectrum: $^{31}P\text{-}\{^1H\}$ (24 MHz), δ 12.50 p.p.m. [s, ^1J(PtP) 2 822 Hz].

(*iii*) *Preparation of* $[Pd\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^t)(PEt_3)]$ (**5c**)·0.5CH_2Cl_2. t-Butyl isocyanide (0.008 g, 0.095 mmol) in dichloromethane (*ca.* 5 cm^3) was added dropwise to a stirred solution of $[Pd\{CH(COPh)S(O)_2CH(COPh)\}(PEt_3)_2]$ (**3d**) (0.060 g, 0.095 mmol) in dichloromethane (20 cm^3), and the solution evaporated to dryness to afford a yellow oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of light petroleum (50 cm^3) afforded pale yellow *microcrystals* of complex (**5c**)·0.5CH_2Cl_2 (0.044 g, 72%), m.p. 74—76 °C; ν(CN) at 2 196s; ν(SO_2) at 1 119vs and 1 300s cm^{-1}. N.m.r. spectra: ^1H (300 MHz), δ 8.29—7.27 (m, 10 H, Ph), 5.30 (s, 1 H, CH_2Cl_2), 4.88 [d, Pd–CH, ^3J(PH) *trans* 8.51], 4.37 [d, 1 H, Pd–CH, ^3J(PH) *cis* 6.18 Hz], 1.74—1.41 (m, 6 H, CH_2, PEt_3), 1.15—0.95 (m, 9 H, CH_3, PEt_3), and 1.08 (s, 9 H, Bu^t); $^{31}P\text{-}\{^1H\}$ (24 MHz), δ 19.36 p.p.m. (s).

(*b*) *With excess of alkyl isocyanide*. (*i*) *Preparation of* $[Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^t\}(CNBu^t)(PPh_3)]$ (**6a**)·0.5CH_2Cl_2. A solution of complex (**3c**)·CH_2Cl_2·0.5H_2O (0.29 g, 0.26 mmol) in dichloromethane (25 cm^3) with Bu^tNC (0.10 g, 1.2 mmol) was refluxed for 4 h. The mixture was evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of light petroleum (50 cm^3) afforded pale yellow *microcrystals* of complex (**6a**)·0.5CH_2Cl_2 (0.19 g, 76%). Slow recrystallisation from dichloromethane–light petroleum yielded pale yellow *prisms* (Found: C, 55.4; H, 5.1; N, 2.9.

$C_{44}H_{45}N_2O_4PPtS\cdot0.5CH_2Cl_2$ requires C, 55.3; H, 4.8; N, 2.9%), m.p. 168—171 °C with gas evolution; ν(NH) at 3 054m; ν(C≡N) at 2 186vs; $\nu_{max.}$(1 700—1 500 cm^{-1}) at 1 660s, 1 582s, 1 570s, and 1 526vs; $\nu(SO_2)$ at 1 125s and 1 307vs cm^{-1}. N.m.r. spectra: ^{1}H (400 MHz), δ 13.33 {d, br, 1 H, NH, ^{3}J(PtH) 93.6, ^{4}J(PH) 14.3, readily exchanged on shaking with [$^{2}H_2$]water containing a trace of sodium[$^{2}H_1$]hydroxide}, 7.95—6.96 (m, 25 H, Ph), 5.32 (s, 1 H, CH_2Cl_2), 4.81 [d, 1 H, Pt–CH, ^{3}J(PH) 11.2, ^{2}J(PtH) 80.0], 1.63 (s, 9 H, Bu^t), and 0.92 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (100 MHz), δ 194.9 [s, CH–*C*OPh, ^{2}J(PtC) not discernible], 188.1 [d, $\bar{C}$-*C*OPh, ^{3}J(PtC) *ca.* 65.4, ^{4}J(PC) 3.4], 186.7 [d, C=N, ^{2}J(PC) 113.2, ^{1}J(PtC) not discernible], 120.8 [s, $\bar{C}$, ^{2}J(PtC) and ^{3}J(PC) not discernible], 69.10 [d, Pt–CH, ^{1}J(PtC) 614.0, ^{2}J(PC) 3.83], 58.35 (s, C, Bu^t), 54.86 (s, C, Bu^t), 31.24 (s, Me, Bu^t), and 28.83 p.p.m. (s, Me, Bu^t); ^{31}P-{^{1}H} (24 MHz), δ 15.73 p.p.m. [s, ^{1}J(PtP) 1 968 Hz].

(*ii*) *Preparation of* $[Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^t\}(CNBu^t)(PMe_2Ph)]$ (**6b**)$\cdot0.5H_2O$. A solution of $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PMe_2Ph)_2]$ (**3e**)$\cdot CH_2Cl_2$ (0.13 g, 0.152 mmol) in dichloromethane (15 cm^3) with Bu^{t}NC (0.10 g, 1.2 mmol) was refluxed for 1 h. The mixture was evaporated to dryness under reduced pressure to give a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 2 cm^3) followed by addition of light petroleum (*ca.* 50 cm^3) afforded pale yellow *microcrystals* of complex (**6b**)$\cdot0.5H_2O$ (0.101 g, 82%) (Found: C, 50.4; H, 5.2; N, 3.35. $C_{34}H_{41}N_2O_4PPtS$ requires C, 51.1; H, 5.2; N, 3.5%), m.p. 139—140 °C; ν(NH) at 3 054w; ν(C≡N) at 2 204vs; $\nu_{max.}$(1 700—1 500 cm^{-1}) at 1 661s, 1 583s, 1 568s, and 1 527vs; $\nu(SO_2)$ at 1 124s and 1 308vs cm^{-1}. N.m.r. spectra: ^{1}H (400 MHz), δ 13.24 [d, br, 1 H, NH, ^{3}J(PtH) 85.5, ^{4}J(PH) 14.5], 7.95—7.13 (m, 15 H, Ph), 5.01 [d, 1 H, Pt–CH, ^{3}J(PH) 11.2, ^{2}J(PtH) 81.7], 1.83 (s, br, 1 H, H_2O), 1.70 [d, 3 H, Me, PMe_2Ph, ^{2}J(PH) 9.5], 1.57 [d, 3 H, Me, PMe_2Ph, ^{2}J(PH) 9.5], 1.37 (s, 9 H, Bu^t), and 1.28 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (75.5 MHz), δ 194.92 [s, CH–*C*OPh, ^{2}J(PtC) 34.7], 189.45 [d, C=N, ^{2}J(PC) 114.5, ^{1}J(PtC) 798.1], 188.51 [d, $\bar{C}$-*C*OPh, ^{4}J(PC) *ca.* 1.9, ^{3}J(PtC) 62.3], 120.31 [s, $\bar{C}$, ^{2}J(PtC) *ca.* 30], 66.81 [d, Pt–CH, ^{2}J(PC) 3.8, ^{1}J(PtC) 569.8], 58.88 [s, C, Bu^t, ^{3}J(PtC) *ca.* 9.1], 54.85 [d, C, Bu^t, ^{4}J(PC) 3.8, ^{3}J(PtC) 24.5], 31.40 (s, Me, Bu^t), 29.46 (s, Me, Bu^t), 15.02 [d, Me, PMe_2Ph, ^{1}J(PC) 34.4, ^{2}J(PtC) 28.3], and 14.38 p.p.m. [d, Me, PMe_2Ph, ^{1}J(PC) 34.4, ^{2}J(PtC) 30.2]; ^{31}P-{^{1}H} (24 MHz), δ −14.92 p.p.m. [s, ^{1}J(PtP) 1 919 Hz].

(*iii*) *Preparation of* $[Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^n)(PPh_3)]$ (**6c**)$\cdot0.5CH_2Cl_2$. A solution of complex (**3c**)$\cdot CH_2Cl_2\cdot0.5H_2O$ (0.30 g, 0.27 mmol) in dichloromethane (20 cm^3) with Bu^{n}NC (0.1 cm^3, 0.96 mmol) was refluxed for 1 h. Work-up as in (*ii*) above afforded white *microcrystals* of complex (**6c**)$\cdot0.5CH_2Cl_2$ (0.176 g, 68%) (Found: C, 55.5; H, 4.9; N, 2.9. $C_{44}H_{45}N_2O_4PPtS\cdot0.5CH_2Cl_2$ requires C, 55.3; H, 4.8; N, 2.9%), m.p. 133—136 °C; ν(C≡N) at 2 260vs; ν(C=N/C=O) at 1 686s and 1 560vs(br); $\nu(SO_2)$ at 1 124vs and 1 306s cm^{-1}. N.m.r. spectra: ^{1}H (300 MHz), δ 12.55 [m, br, 1 H, NH, ^{3}J(PtH) *ca.* 78, ^{4}J(PH) and ^{3}J(HH) not discernible], 5.25 (s, 1 H, CH_2Cl_2), and 5.02 [d, 1 H, Pt–CH, ^{3}J(PH) 10.7, ^{2}J(PtH) 75.0]; ^{31}P-{^{1}H} (24 MHz), δ 14.52 p.p.m. [s, ^{1}J(PtP) 1 968 Hz].

(*iv*) *Preparation of* $[Pt\{CH(CO_2Me)S(O)_2\bar{C}(CO_2Me)C{=}\overset{+}{N}HBu^t\}(CNBu^t)(PPh_3)]$ (**6d**)$\cdot CH_2Cl_2$. A solution of $[Pt\{CH(CO_2Me)S(O)_2CH(CO_2Me)\}(PPh_3)_2]$ (**3f**)$\cdot CH_2Cl_2$ (0.20 g, 0.197 mmol) in dichloromethane (20 cm^3) with Bu^{t}NC (0.10 g, 1.2 mmol) was refluxed for 1 h. Work-up as in (*ii*) above afforded white *microcrystals* of complex (**6d**)$\cdot CH_2Cl_2$ (0.163 g. 90%) (Found: C, 46.0; H, 5.0; N, 3.05. $C_{34}H_{41}N_2O_6PPtS\cdot CH_2Cl_2$ requires C, 45.9; H, 4.7; N, 3.1%), m.p. 215—218 °C (decomp.); ν(C≡N) at 2 084vs; $\nu_{max.}$(1 700—1 500 cm^{-1}) at 1 672vs, 1 580vs, and 1 500vs; $\nu(SO_2)$ at 1 140vs and 1 297vs cm^{-1}. N.m.r. spectra: ^{1}H (90 MHz), δ 10.5 [d, br, 1 H, NH, ^{3}J(PtH) *ca.* 95, ^{4}J(PH) *ca.* 14], 7.8—7.2 (m, 15 H, Ph), 5.25 (s, 2 H, CH_2Cl_2), 3.8 [d, 1 H, Pt–CH, ^{2}J(PtH) 84.0, ^{3}J(PH) 11.4], 3.75 (s, 3 H, Me, CO_2Me), 3.4 [s, 3 H, Me, CO_2Me], 1.5 (s, 9 H, Bu^t), and 1.0 (s, 9 H, Bu^t); ^{31}P-{^{1}H} (24 MHz), δ 16.34 p.p.m. [s, ^{1}J(PtP) 1 997 Hz].

Preparation of $[Pd\{CH_2C(O)\bar{C}(CO_2Me)C{=}\overset{+}{N}HBu^t\}(CNBu^t)_2]$ (**12**).—A solution of $[Pd\{\eta^3\text{-}CH_2C(O)CH(CO_2Me)\}(bipy)]$ (**11**) (0.182 g, 0.484 mmol) in dichloromethane (20 cm^3) with excess of Bu^{t}NC (0.2 cm^3, 1.78 mmol) was refluxed for 1 h. Evaporation to *ca.* 2 cm^3 under reduced pressure followed by addition of light petroleum (50 cm^3) afforded pale yellow *microcrystals* of complex (**12**) (0.195 g, 86%). N.m.r. spectra: ^{1}H (300 MHz), δ 10.68 (s, br, 1 H, NH), 3.69 (s, 3 H, CO_2Me), 2.75 (s, 2 H, Pd–CH_2), 1.54 (s, 9 H, Bu^t), and 1.49 (s, 18 H, Bu^t); ^{13}C-{^{1}H} (75.5 MHz), δ 206.73 [s, C=N, d in ^{13}C spectrum, ^{2}J(CH) 5.3], 199.46 (s, *C*O_2Me), 167.24 (s, CH_2*C*OC), 138.36 (s, br, Pd–CN), 136.09 (s, br, Pd–CN), 105.85 [s, *C*-CO_2Me, apparent d in ^{13}C spectrum but *J*(CH) not discernible], 56.78 (s, C, Bu^t), 56.50 (s, C, Bu^t), 52.43 (s, C, Bu^t), 49.11 [s, CO_2*Me*, q in ^{13}C spectrum, ^{1}J(CH) 145.4], 37.44 [s, Pd–CH_2, t in ^{13}C spectrum, ^{1}J(CH) 137.1 Hz], 29.90 (s, Me, Bu^t), 29.40 (s, Me, Bu^t), and 29.10 p.p.m. (s, Me, Bu^t). The complex decomposed quickly on standing, and could not be obtained analytically pure.

Reaction of $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^t)(PPh_3)]$ (**5a**) *with n-Butyl Isocyanide.*—Complex (**5a**) was prepared from (**3c**)$\cdot CH_2Cl_2\cdot0.5H_2O$ (0.20 g) and Bu^{n}NC (0.015 g) as described previously, and the solution evaporated to dryness under reduced pressure to afford a pale yellow oil which was triturated with light petroleum (10 cm^3) to remove triphenylphosphine. The residual solid was dissolved in dichloromethane (25 cm^3) and Bu^{n}NC (0.015 g, 0.181 mmol) in dichloromethane (10 cm^3) was added. The mixture was refluxed for 1 h and evaporated to *ca.* 1 cm^3 under reduced pressure. Addition of light petroleum gave pale yellow *microcrystals* of $[Pt\{CH(COPh)S(O)_2\bar{C}(COPh)C{=}\overset{+}{N}HBu^n\}(CNBu^t)(PPh_3)]$ (**13**)$\cdot CH_2Cl_2$ (0.157 g, 88%). Slow recrystallisation from dichloromethane–light petroleum gave colourless *prisms* (Found: C, 53.4; H, 4.7; N, 2.75. $C_{44}H_{45}N_2O_4PPtS\cdot CH_2Cl_2$ requires C, 53.6; H, 4.7; N, 2.8%), m.p. 139—143 °C; ν(NH) at 3 040w; ν(C≡N) at 2 186vs; $\nu_{max.}$(1 700—1 500 cm^{-1}) at 1 650s and 1 534vs(br); $\nu(SO_2)$ at 1 100vs and 1 284(br) cm^{-1}. N.m.r. spectra: ^{1}H (400 MHz), δ 12.55 [m, br, 1 H, NH, ^{4}J(PH) and ^{3}J(HH) not discernible, ^{3}J(PtH) 75.8], 8.39—6.93 (m, 25 H, Ph), 5.28 (s, 2 H, CH_2Cl_2), 4.87 [d, 1 H, Pt–CH, ^{3}J(PH) 10.8, ^{2}J(PtH) 72.8], 3.75 (m, 2 H, CH_2, Bu^n), 3.53 (m, 2 H, CH_2, Bu^n), 1.85 (m, 2 H, CH_2, Bu^n), 1.56 (m, 2 H, CH_2, Bu^n), 1.04 (s, 9 H, Bu^t), and 1.01 [t, 3 H, Me, Bu^n, ^{3}J(HH) 7.4]; ^{31}P-{^{1}H} (24 MHz), δ 14.52 p.p.m. [s, ^{1}J(PtP) 1 972 Hz]. Crystals of (**13**)$\cdot CHCl_3$ suitable for an *X*-ray study were obtained by slow diffusion of diethyl ether and hexane into a chloroform solution of (**13**).

Reaction of $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(CNBu^n)(PPh_3)]$ (**5b**) *with t-Butyl Isocyanide.*—Complex (**5b**) was prepared from (**3c**)$\cdot CH_2Cl_2\cdot0.5H_2O$ (0.20 g) and Bu^{t}NC (0.015 g) as described previously, and the solution evaporated to dryness under reduced pressure to afford a pale yellow oil which was triturated with light petroleum (10 cm^3) to remove PPh_3. The residual solid was dissolved in dichloromethane (25 cm^3) and Bu^{t}NC (0.015 g, 0.181 mmol) in dichloromethane (10 cm^3) was added. The mixture was refluxed for 1 h and

Table 3. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.195 96(2)	0.183 28(7)	0.412 20(3)	C(31)	0.093 3(5)	0.070 3(12)	0.459 6(8)
P	0.124 93(12)	0.230 4(4)	0.456 97(19)	C(32)	0.117 9(5)	−0.032 1(12)	0.511 3(8)
S	0.280 96(13)	0.076 1(4)	0.538 29(19)	C(33)	0.097 2(5)	−0.162 8(12)	0.514 9(8)
O(1)	0.323 69(29)	0.101 9(11)	0.601 9(5)	C(34)	0.051 8(5)	−0.191 1(12)	0.466 8(8)
O(2)	0.251 9(3)	−0.042 3(11)	0.552 9(5)	C(35)	0.027 1(5)	−0.088 7(12)	0.415 1(8)
O(3)	0.285 4(3)	0.400 4(11)	0.471 7(5)	C(36)	0.047 9(5)	0.042 0(12)	0.411 5(8)
O(4)	0.355 4(3)	0.045 6(14)	0.361 9(5)	C(41)	0.276 76(29)	0.437 5(11)	0.608 1(4)
C(1)	0.240 8(4)	0.218 4(12)	0.526 6(6)	C(42)	0.279 04(29)	0.581 8(11)	0.602 4(4)
C(2)	0.295 3(4)	0.072 2(15)	0.440 7(7)	C(43)	0.286 32(29)	0.662 9(11)	0.673 9(4)
C(3)	0.260 2(4)	0.133 4(15)	0.379 4(8)	C(44)	0.291 32(29)	0.599 6(11)	0.751 2(4)
C(4)	0.269 7(5)	0.355 4(13)	0.529 9(7)	C(45)	0.289 03(29)	0.455 2(11)	0.756 9(4)
C(5)	0.341 6(5)	0.024 4(18)	0.427 8(8)	C(46)	0.281 76(29)	0.374 2(11)	0.685 4(4)
C(6)	0.157 1(4)	0.121 0(16)	0.310 5(7)	C(51)	0.375 0(3)	−0.057 7(12)	0.491 3(5)
C(7)	0.098 5(6)	0.017 3(28)	0.173 4(9)	C(52)	0.424 0(3)	−0.026 8(12)	0.505 5(5)
C(8)	0.127 6(7)	−0.028(4)	0.115 4(12)	C(53)	0.456 9(3)	−0.109 8(12)	0.558 7(5)
C(9)	0.064 3(10)	−0.079(4)	0.195 2(13)	C(54)	0.440 8(3)	−0.223 7(12)	0.597 6(5)
C(10)	0.069 6(10)	0.148(4)	0.136 3(14)	C(55)	0.391 7(3)	−0.254 6(12)	0.583 4(5)
C(11)	0.128 3(3)	0.309 1(11)	0.558 1(4)	C(56)	0.358 8(3)	−0.171 6(12)	0.530 2(5)
C(12)	0.154 5(3)	0.431 3(11)	0.578 0(4)	C(101)	0.401 7(17)	0.318(5)	0.660(3)
C(13)	0.156 7(3)	0.493 7(11)	0.655 0(4)	C(201)	0.242 0(6)	0.250 9(23)	0.239 9(9)
C(14)	0.132 6(3)	0.433 9(11)	0.712 0(4)	C(202)	0.258 3(9)	0.245(3)	0.169 8(11)
C(15)	0.106 4(3)	0.311 7(11)	0.692 2(4)	C(203)	0.297 7(8)	0.165(3)	0.142 0(10)
C(16)	0.104 2(3)	0.249 3(11)	0.615 2(4)	C(204)	0.324 5(8)	0.214(4)	0.091 5(15)
C(21)	0.083 2(3)	0.345 4(11)	0.391 9(6)	N(1)	0.271 8(4)	0.162 6(16)	0.306 9(6)
C(22)	0.095 2(3)	0.402 3(11)	0.321 0(6)	N(2)	0.132 1(4)	0.070 7(14)	0.250 5(6)
C(23)	0.063 7(3)	0.494 5(11)	0.272 0(6)	Cl(1)	0.432 4(5)	0.353 8(14)	0.590 8(7)
C(24)	0.020 2(3)	0.529 7(11)	0.293 8(6)	Cl(2)	0.421 4(4)	0.394 1(20)	0.755 4(10)
C(25)	0.008 2(3)	0.472 9(11)	0.364 7(6)	Cl(3)	0.440 0(11)	0.222(3)	0.700 1(20)
C(26)	0.039 7(3)	0.380 8(11)	0.413 7(6)				

evaporated to 1 cm^3 under reduced pressure. Addition of light petroleum afforded a pale yellow microcrystalline *solid* (0.196 g, 86%) which was identified as (**13**)·CH_2Cl_2 from its ^1H and ^{31}P-{^1H} n.m.r. spectra.

Miscellaneous Reactions of [Pt{CH(COPh)S(O)$_2$CH(COPh)}(PPh$_3$)$_2$] (**3c**)·CH_2Cl_2·0.5H_2O.—A sample of complex (**3a**)·CH_2Cl_2·0.5H_2O was heated to 250 °C in air for 10 min, to afford a brownish glass on cooling, which was shown from its ^{31}P-{^1H} n.m.r. spectrum to contain unchanged (**3c**).

Reaction with hexafluoroacetone. An excess of hexafluoroacetone was condensed onto a frozen (−196 °C) solution of complex (**3c**)·CH_2Cl_2·0.5H_2O (0.20 g) in dichloromethane (20 cm^3) contained in a Carius tube. The tube was sealed, stirred at room temperature for 48 h, cooled, opened, and the contents evaporated to dryness under reduced pressure to afford a colourless oil. Recrystallisation from dichloromethane–light petroleum afforded white *needles* of (**3c**)·C(CF_3)$_2$(OH)$_2$ (0.201 g, 93%) [Found: C, 54.5; H, 3.8. $C_{52}H_{42}O_4P_2PtS$·C(CF_3)$_2$(OH)$_2$ requires C, 54.9; H, 3.7%], m.p. 172—176 °C. Selected n.m.r. spectroscopic data: ^1H (400 MHz), δ 4.82 [d, second order, 2 H, Pt–CH, $|^3J$(PH) *trans* + ^3J(PH) *cis* 9.49, ^2J(PtH) 61.27]; ^{31}P-{^1H} (24 MHz), δ 11.90 p.p.m. [s, ^1J(PtP) 2 876 Hz]; ^{19}F-{^1H} (94 MHz), δ 1.4 p.p.m. (s).

Reaction with (phenylsulphonyl)acetic acid. A solution of (phenylsulphonyl)acetic acid (0.013 g, 0.065 mmol) in dichloromethane (10 cm^3) was added to a stirred solution of complex (**3c**)·CH_2Cl_2·0.5H_2O (0.070 g, 0.063 mmol) in dichloromethane (10 cm^3). The solution was stirred for 20 min, and evaporated to dryness under reduced pressure to afford a white *solid* which was shown by ^{31}P-{^1H} n.m.r. spectroscopy to contain unreacted (**3c**). The solid was dissolved in dichloromethane (20 cm^3), refluxed for 30 min, and evaporated to dryness under reduced pressure to afford a white *solid* which was found to consist of a 1:1 mixture of unreacted (**3c**) and the bis(carboxylate) complex *cis*-[Pt{OC(O)CH$_2$SO$_2$Ph}$_2$(PPh$_3$)$_2$] (**15**) by comparison of its ^{31}P-{^1H} n.m.r. spectrum with those of authentic samples of (**3c**) and (**15**) (see below).

Preparation of [Pt{OC(O)CH$_2$SO$_2$Ph}$_2$(PPh$_3$)$_2$] (**15**)·CH_2Cl_2·H_2O.—Triphenylphosphine (0.14 g, 0.534 mmol), (phenylsulphonyl)acetic acid (0.107 g, 0.535 mmol), and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession to a stirred solution of [PtCl$_2$(cod)] (0.10 g, 0.267 mmol) in dichloromethane (20 cm^3), and the mixture was refluxed for 30 min. It was filtered to afford a pale yellow solution which was evaporated to dryness under reduced pressure to afford a pale yellow oil. Crystallisation of the oil from dichloromethane–light petroleum gave a pale yellow microcrystalline *solid* which was recrystallised from dichloromethane–light petroleum to afford white *needles* of complex (**15**)·CH_2Cl_2·H_2O (0.201 g, 62%) (Found: C, 52.3; H, 4.2. $C_{52}H_{44}O_8P_2PtS_2$·CH_2Cl_2·H_2O requires C, 52.1; H, 4.0%), m.p. 132—134 °C. N.m.r. spectra: ^1H (90 MHz), δ 7.9—7.1 (m, 40 H, Ph), 5.3 (s, 2 H, CH_2Cl_2), 3.36 (s, 4 H, CH_2), and 1.8 (s, br, 2 H, H_2O); ^{31}P-{^1H} (24 MHz), δ 5.0 p.p.m. [s, ^1J(PtP) 3 877 Hz].

Crystal Structure Determination.—Crystals of complex (**13**)·$CHCl_3$ were obtained by slow diffusion of hexane into a chloroform solution of (**13**). A white irregular rectangle of approximate dimensions 0.056 × 0.30 × 0.14 mm was mounted in air. The cell dimensions were determined from oscillation photographs about the *b* axis and from optimised counter angles for zero- and upper-layer reflections. Data were collected on a Stöe STADI-2 Weissenberg diffractometer using an ω-scan technique in the range $7 \leqslant 2\theta \leqslant 54°$. The 4 019 unique reflections collected from Weissenberg layers *h*(0—10)*l* having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX.[22]

Crystal data. $C_{44}H_{45}N_2O_4PPtS$·$CHCl_3$, M = 1 011.3, monoclinic, space group $P2_1/n$, a = 28.337(2), b = 9.625(2), c =

16.507(1) Å, $\beta = 101.71(5)^\circ$, $U = 4\,408.45$ Å^3, $Z = 4$, $D_c = 1.57$ g cm^{-3}, $F(000) = 2\,059.8$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 33.29 cm^{-1}.

The molecular structure was solved by conventional Patterson and Fourier difference techniques. Scattering factors were taken from ref. 23. An absorption correction was applied, the maximum and minimum transmission factors being 0.8439 and 0.6366. In the final stages of blocked-matrix least-squares refinements all non-hydrogen atoms were given anisotropic thermal parameters. All phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The hydrogen atoms of the phenyl rings were refined at calculated positions [C–H 1.08(5) Å]. Final cycles employed a weighting factor $w = k/(\sigma^2F + gF^2)$ where $k = 2.0865$ and $g = 0.000\,127$. Final $R[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.0661 and 0.0530 respectively. The atomic co-ordinates for the structure are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank the S.E.R.C. for support and for the provision of high-field n.m.r. facilities, Johnson Matthey plc for the generous loan of platinum metal salts, and Dr. O. W. Howarth (University of Warwick) and Miss M. Robinson (University of Leicester) for high-field n.m.r. measurements.

References

1 Part 2, W. Henderson, R. D. W. Kemmitt, L. J. S. Prouse, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1989, 259.
2 R. D. W. Kemmitt, P. McKenna, L. J. S. Prouse, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1989, 345.
3 W. Henderson, M. D. Jones, and R. D. W. Kemmitt, unpublished work.
4 K. W. Chiu, J. Fawcett, W. Henderson, R. D. W. Kemmitt, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1987, 733.
5 S. F. Dyke, A. J. Floyd, M. Sainsbury, and R. S. Theobald, 'Organic Spectroscopy,' 2nd edn., Longman, London and New York, 1978, p. 88.
6 P. M. Treichel and K. P. Wagner, *J. Organomet. Chem.*, 1973, **61**, 415.
7 H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 503.
8 R. J. Klinger, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 2147.
9 P. M. Treichel and R. W. Hess, *J. Am. Chem. Soc.*, 1970, **92**, 4731.
10 P. M. Treichel, K. P. Wagner, and R. W. Hess, *Inorg. Chem.*, 1973, **12**, 1471.
11 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1873.
12 S. Otsuka and K. Ataka, *J. Chem. Soc., Dalton Trans.*, 1976, 327.
13 R. Bertani, C. B. Castellani, and B. Crociani, *J. Organomet. Chem.*, 1984, **269**, C15.
14 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
15 P. G. Jones, *Chem. Soc. Rev.*, 1984, **13**, 157.
16 R. M. Dodson, E. H. Jancis, and G. Close, *J. Org. Chem.*, 1970, **35**, 2520.
17 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1978, 744.
18 T. Glonek and J. R. van Wager, *J. Magn. Reson.*, 1974, **13**, 390.
19 W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Am. Chem. Soc.*, 1961, **83**, 4019.
20 J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
21 N. Yanase, Y. Nakamura, and S. Kawaguchi, *Inorg. Chem.*, 1980, **19**, 1575.
22 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1976.
23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

Received 8*th June* 1989; *Paper* 9/02419K