DOI: 10.1002/ejic.200800333

Selective Cleavage by Acids of One Metal–Carbon σ-Bond of a Bis(*ortho*-platinated) Triarylphosphane: A ^{31}P NMR *trans*-Influence Series Based on the Unit Pt(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)

Martin A. Bennett,[a] Suresh K. Bhargava,*[b] Steven H. Privér,[b] and Anthony C. Willis[a]

Keywords: Platinum / *ortho*-Metallated complexes / *trans*-Influence

Treatment of the bis(chelate) complex *cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh_2)$_2$] (**1**) with strong acids causes selective cleavage of one of the metal–aryl bonds to give *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = Cl (**2**), Br (**3**), I (**4**), ONO_2 (**5**) and $OCOCF_3$ (**6**)], from which a series of neutral and cationic derivatives can be derived by metathetical reactions. The complexes **2** and **6** rearrange spontaneously to the corresponding *trans* isomers, this reaction being promoted by CO. The *J*(Pt-P) values for the phosphorus atom of the four-membered ring can be ordered to establish a *trans*-influence series of anionic ligands X and neutral ligands L, which correlates well with, but is more extensive than, that based earlier on PtMe(dppe) complexes. Single-crystal X-ray structural analysis of *trans*-[Pt(κ^1-$OCOCF_3$)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (*trans*-**6**), *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = Cl (**2**), CN (**11**), Me (**43**) and C_6F_5 (**45**)], and [Pt(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)$_2$]BF_4 (**34**) show these complexes to have distorted square-planar geometry. The Pt–P distances to the phosphorus atom of the four-membered ring in **2**, **11**, **43** and **45** broadly follow the trend of *J*(Pt–P) values, Cl^- being placed near the bottom and Me^- near the top of the *trans*-influence series, but the corresponding Pt–P distance in **34** is out of line. The Pt–P distances to PPh_2-4-tol *cis* to X or L tend to decrease with increasing *trans*-influence of X or L, in agreement with previous indications of a ligand *cis*-influence that runs opposite to the *trans*-influence.

1. Introduction

The *trans*-influence of a ligand was first defined by Pidcock, Richards and Venanzi[1] as the extent to which that ligand weakens the bond *trans* to it in the ground state of a complex, particularly a planar platinum(II) complex; it is to be distinguished from the *trans*-effect, which refers to the rates of replacement of groups *trans* to the ligand, i.e., a kinetic effect.[2–4] Although many physical techniques have been employed to study the *trans*-influence,[5] one of the most versatile remains that used by Pidcock et al., namely, the evaluation of ^{195}Pt-^{31}P NMR coupling constants, *J*(Pt-P). It is assumed that this coupling is determined by the Fermi contact term, i.e., by the interaction between the nuclear spin and the s-electrons, which alone have finite density at the nucleus. The coupling is given by the proportionality

$$^1J(\text{Pt-P}) \propto \gamma_{Pt}\gamma_P(\Delta E)^{-1}a_{Pt}^2a_P^2|\Psi_{Pt(0)}|^2|\Psi_{P(0)}|^2$$

where γ_{Pt}, γ_P are the magnetogyric ratios for the two spin-1/2 nuclei, ΔE is a mean singlet-triplet excitation energy, a_{Pt}^2, a_P^2 are the s-characters of the hybrid orbitals used by the respective atoms in the Pt–P bond, and $|\Psi_{Pt(0)}|^2$, $|\Psi_{P(0)}|^2$ are the squares of the magnitudes of the valence-state s-orbitals evaluated at the parent nucleus.

In most cases, it appears that a_{Pt}^2 is the dominant influence, so that changes in *J*(Pt-P) reflect primarily variations in the s-character of the Pt–P bond; ligands of high *trans*-influence make a high demand on Pt 6s-orbital character. This approach has been applied to various P-donor complexes of platinum(II) and used to construct *trans*-influence series.[6–10] It is also of interest to correlate these series with those acquired by the ordering of parameters obtained by other physical techniques, in particular, with bond lengths obtained by X-ray crystallography[11–18] and with other direct and indirect NMR coupling constants, such as ^1J(Pt-H), ^1J(Pt-C), ^2J(Pt-CH_3) and ^2J(Pt-CF_3).[5,19,20]

Although there are numerous X-ray crystallographic studies on planar platinum(II) complexes containing tertiary phosphanes, only in a series of *cis*-[$PtCl_2$(PEt_3)(L)] complexes has a systematic comparison of ^1J(Pt-P) with (Pt-Cl) bond length data been carried out to obtain information about *trans*- and *cis*-influences.[11–14] We describe here a series of *ortho*-metallated triarylphosphane complexes of platinum(II) whose ^{31}P NMR spectroscopic data provide a *trans*-influence series for a wide range of neutral and an-

---

[a] Research School of Chemistry, Australian National University,
Canberra, ACT 0200, Australia
Fax: +61-2-6125 3216
E-mail: bennett@rsc.anu.edu.au
[b] School of Applied Sciences (Applied Chemistry), RMIT University,
GPO Box 2476V, Melbourne, Victoria 3001, Australia
Fax: +61-3-9925 3365
E-mail: suresh.bhargava@rmit.edu.au

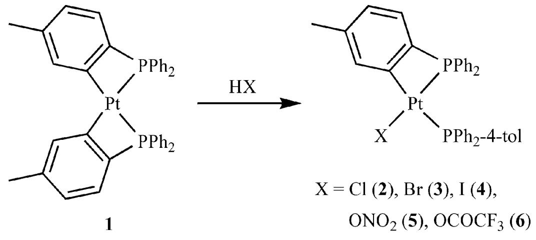
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

ionic ligands. The results can be compared with those obtained by single-crystal X-ray structural determinations on selected members.

2. Results and Discussion

2.1 Formation of *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (X = Cl, Br, I, ONO_2, $OCOCF_3$)

When a THF (for definitions of abbreviations, see Experimental Section) solution of the bis(chelate) complex *cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh_2)$_2$] (**1**),[21] which contains two four-membered rings, is treated with a strong acid, such as HCl, HBr, HI, HNO_3 or CF_3COOH, one of the Pt–aryl bonds is cleaved selectively to give *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = Cl (**2**), Br (**3**), I (**4**), ONO_2 (**5**) and $OCOCF_3$ (**6**)] in high yield (Scheme 1). Also formed in a small amount is the product derived by cleavage of both Pt–C bonds, [PtX_2(PPh_2-4-tol)$_2$], which is easily removed by column chromatography. In the case of HI, a significant amount of the diiodoplatinum(IV) complex [PtI_2(κ^2-C_6H_3-5-Me-2-PPh_2)$_2$][21] also formed, possibly arising from the addition of traces of iodine in the HI to **1**. Complexes **3** and **4** can also be prepared by metathesis of **2** with LiBr or NaI, respectively, in acetone. All the complexes except **5** show the expected molecular ion peak in their ES mass spectra.



Scheme 1.

Evidence for the presence of only one four-membered ring in complexes **2**–**6** is provided by spectroscopic data, particularly the ^{31}P NMR spectra, which consist of a pair of doublets, with ^{195}Pt satellites, at $\delta \approx 20$ and –60 to –80 ppm. The former is unexceptional for triarylphosphanes coordinated to platinum(II), while the highly shielded resonance is typical of a phosphorus atom in a strained four-membered chelate ring.[22] The IR spectrum of **2** shows typical *ortho*-metallation bands at 1569 and 725 cm^{-1},[23,24] together with a band at 314 cm^{-1} assignable to ν(PtCl) for Cl *trans* to a tertiary phosphane in a planar platinum(II) complex.[25] The pair of doublets in the ^{31}P NMR spectrum at δ = 18.5 and –72.8 ppm [*J*(P-P) = 5.8 Hz] is associated with Pt-P coupling constants of 1990 Hz and 3392 Hz, respectively, corresponding to P *trans* to the η^1-carbon atom and the chloride ion.[9,26] The structure of **2** has been confirmed by a single-crystal X-ray diffraction study (see later).

The ^{31}P NMR spectra of the complexes **3**–**6** are similar to that of **2**, the data being collected in Table 1. The IR

Table 1. ^{31}P NMR spectroscopic data for neutral *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] complexes and *cis*-[PtL(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)]BF_4 salts.[a–c]

X or L	$\delta(P_A)$	^1J(Pt-P)	^2J(P-P)	$\delta(P_B)$	^1J(Pt-P)
L = Ph_3PO (**18**)[d]	23.4	1948	[e]	–82.3	3835
L = THF (**17**)	23.6	2129	6.4	–81.4	3652
X = ONO_2 (**5**)	21.5	2068	7.0	–83.9	3574
X = $OCOCF_3$ (**6**)	21.5	2041	5.7	–83.0	3507
L = MeCN (**26**)	17.9	1956	8.6	–83.0	3487
X = Cl (**2**)	18.5	1990	5.9	–72.8	3392
X = F (**7**)[f]	19.0[g]	1999	4.6	–81.8	3380[h]
X = Br (**3**)	17.9	1998	5.4	–73.6	3365
L = NEt_3 (**20**)	22.8	1928	4.8	–81.9	3314
X = NCS (**14**)[i]	16.7	1932	7.6[j]	–80.0	3283
L = PhC≡CPh (**42**)	19.4	1903	7.0	–70.0	3274
X = OCOPh (**10**)	21.3	2056	7.7	–81.6	3272
L = MeC≡CMe (**41**)	17.0	1923	6.9	–70.3	3260
X = NCO (**13**)	16.5	1932	7.4[j]	–78.0	3243
X = OCOMe (**9**)	21.5	2044	6.4	–81.6	3236
X = N_3 (**12**)	16.9	2023	8.4	–74.4	3207
X = I (**4**)	15.7	2009	4.9	–78.1	3201
X = Ph_3PS (**32**)[k]	16.7	1948	7.7	–71.8	3168
X = Ph_3PSe (**33**)[l]	16.3	1942	7.2	–72.3	3108[m]
L = *o*-$MeC_6H_4NH_2$ (**22**)	17.2	2016	10.0	–80.3	3096
L = $PhNH_2$ (**21**)	16.8	2017	10.2	–80.7	3062
L = *m*-$MeC_6H_4NH_2$ (**23**)	16.7	2028	10.1	–80.7	3055
L = NH_3 (**19**)	17.6	1957	9.6	–78.3	3039
L = *p*-$MeC_6H_4NH_2$ (**24**)	16.6	2056	9.8	–79.7	3011
L = SPh_2 (**29**)	15.1	1949	9.4	–71.5	3002
X = SCN (**14**)[n]	18.8	2041	8.8	–68.2	2923
X = SeCN (**15**)	19.2	2078	8.7	–68.8	2888[o]
L = C_5H_5N (**25**)	18.8	1975	8.3	–83.0	2888
L = THT (**30**)	18.6	2059	11.4	–72.8	2883
L = SMe_2 (**27**)	16.5	2010	10.7	–72.2	2845
L = SEt_2 (**28**)	14.7	1940	10.5	–72.4	2819
X = OH (**8**)	18.1	2006	7.0	–75.8	2802
L = $SbPh_3$ (**36**)	13.8	2032	11.4	–66.6	2765
L = DMSO (**31**)	18.5	2007	[e]	–78.7	2640
L = $AsPh_3$ (**35**)	15.6	2026	13.4	–69.2	2635
L = CO (**39**)	15.0	1832	13.4	–76.5	2599
X = NO_2 (**16**)	18.3	2063	8.6	–86.5	2544
L = ^{t}BuNC (**40**)	14.3	1840	11.7	–73.5	2504
X = CN (**11**)	16.8	1888	11.3	–70.1	2207
L = PPh_2-4-tol (**34**)	16.7	2004	18.0	–67.8	2132
L = $P(OPh)_3$ (**37**)[p]	19.2	1895	14.4	–70.3	2111
L = $P(OMe)_3$ (**38**)[q]	19.2	1894	16.0	–68.3	1969
X = C_6F_5 (**45**)	17.0	1981	11.4	–64.0	1803
X = Me (**43**)	21.6	2123	10.2	–50.7	1122
X = Ph (**44**)	19.6	2071	11.5	–55.9	1041

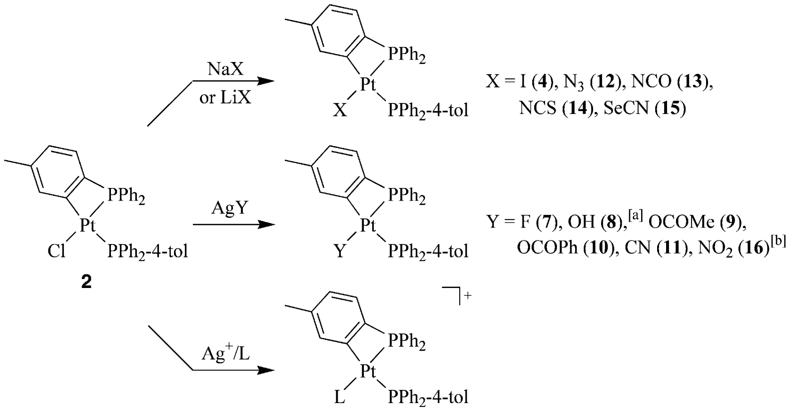
[a] Measured in $CDCl_3$, except where stated otherwise. [b] P_A refers to PPh_2-4-tol, P_B refers to C_6H_3-5-Me-2-PPh_2. [c] Estimated errors in ^2J(P-P) and ^1J(Pt-P) are ±0.5 Hz and ±3 Hz, respectively. [d] $\delta(Ph_3PO)$ = 42.5 ppm, ^{195}Pt satellites not observed. [e] Coupling not observed. [f] In CD_2Cl_2. [g] *J*(P-F) = 26.1 Hz. [h] *J*(P-F) = 161.5 Hz. [i] ^{31}P NMR (CD_2Cl_2, –90 °C): $\delta(P_A)$ = 16.5 [d, *J*(P-P) = 8.2 Hz, *J*(Pt-P) = 1916 Hz] ppm, $\delta(P_B)$ = –78.9 [d, *J*(P-P) = 7.6 Hz, *J*(Pt-P) = 3249 Hz] ppm. [j] Coupling not resolved on P_B resonance (see text). [k] $\delta(Ph_3PS)$ = 41.8 [^3J(P-P) = 6.5, 6.5 Hz, ^2J(Pt-P) = 68.7 Hz] ppm. [l] $\delta(Ph_3PSe)$ = 27.6 [^3J(P-P) = 9.0, 9.0 Hz, ^2J(Pt-P) = 77.0 Hz, *J*(Se-P) = 602 Hz] ppm. [m] *J*(Se-P) = 71.3 Hz. [n] ^{31}P NMR (CD_2Cl_2, –90 °C): $\delta(P_A)$ = 20.4 [d, *J*(P-P) = 10.0 Hz, *J*(Pt-P) = 2088 Hz] ppm, $\delta(P_B)$ = –66.8 [d, *J*(P-P) = 10.0 Hz, *J*(Pt-P) = 2952 Hz] ppm. [o] *J*(Se-P) = 82.2 Hz. [p] $\delta[P(OPh)_3]$ = 91.9 [*J*(P-P) = 596 Hz (*trans*), 26.5 Hz (*cis*), ^1J(Pt-P) = 4914 Hz] ppm. [q] $\delta[P(OMe)_3]$ = 103.1 [*J*(P-P) = 576 Hz (*trans*), 28.0 Hz (*cis*), ^1J(Pt-P) = 4807 Hz] ppm.

spectrum of the nitrato complex **5** contains bands at 1480 and 1272 cm^{-1} due to the asymmetric and symmetric $\nu(NO_2)$ vibrations. The separation ($\Delta\tilde{\nu}$) of 208 cm^{-1} is consistent with the presence of κ^1-ONO_2, as in complexes such as $[Re(ONO_2)(CO)_5]$ and $[Pt(ONO_2)_2L_2]$ (L = substituted pyridine);[27,28] other modes of nitrate coordination generally give larger $\Delta\tilde{\nu}$ values. Similarly, the IR spectrum of the trifluoroacetato complex **6** exhibits bands at 1699 and 1409 cm^{-1} ($\Delta\tilde{\nu}$ = 290 cm^{-1}) arising from the asymmetric and symmetric ν(COO) vibrations, the value of $\Delta\tilde{\nu}$ being indicative of κ^1-$OCOCF_3$;[29–31] values of $\Delta\tilde{\nu}$ less than 200 cm^{-1} are generally associated with chelating and bridging modes of coordination of trifluoroacetate.

When a solution of **2** in $CDCl_3$ is set aside for 24 h, partial isomerisation to the *trans*-isomer (ca. 10%) occurs, as shown by ^{31}P NMR spectroscopy. This process goes to completion under CO in 30 min, presumably being catalysed by reversible opening of the chelate ring and coordination of CO, as suggested also for the CO-catalysed dimerisation of **1**.[21] A similar process occurs even more readily for the nitrato, trifluoroacetato, and benzoato complexes, **5**, **6** and **10**, respectively (see section 2.2.1). Recrystallisation of the trifluoroacetato complex gave *trans*-**6**, whose X-ray structure (see later) confirmed the presence of κ^1-$OCOCF_3$. The *trans*-isomer is formed quantitatively over 24 h from a solution of **6** in C_6D_6 as shown by ^{31}P NMR spectroscopy; under CO, the reaction is complete after 30 min. The ^{31}P NMR spectra of *trans*-**2** and *trans*-**6** consist of a pair of doublets, with ^{195}Pt satellites, in the region of $\delta \approx 25$ (PPh_2-4-tol) and –60 (C_6H_3-5-Me-2-PPh_2) ppm, the coupling constant ^2J(P-P) being ca. 450 Hz; this value is diagnostic of *trans*-tertiary phosphanes in planar platinum(II) complexes.[32] The facile isomerisation of **6**, even in the absence of CO, must arise from the lability of coordinated trifluoroacetate, which can ionise to generate a labile, coordinatively unsaturated, three-coordinate, or four-coordinate, solvent-stabilised, cation. Detailed studies of complexes of the type *cis*-$[Pt(R)(L)(solvent)]^+$ (R = alkyl or aryl, L = tertiary phosphane) have shown that formation of the thermodynamically favoured *trans*-isomer is promoted by electron-donating substituents on the tertiary phosphanes, steric repulsion between the tertiary phosphanes, distortion of the four-coordinate, planar geometry and interaction of the vacant coordination site with β-hydrogen atoms on R.[33]

2.2 Formation of Ligand Derivatives Containing the Unit *cis*-$[Pt(\kappa^2$-C_6H_3-5-Me-2-$PPh_2)(PPh_2$-4-tol$)]$: General Comments

The chloride ion in **2** is readily replaced by a wide range of other anionic or neutral ligands, either by metathesis with the appropriate alkali metal salt, or by abstraction with a silver salt (usually $AgBF_4$) in the presence of a neutral ligand. The results are shown in Scheme 2. Most of the complexes have been isolated in ca. 80–90% yields as colourless or off-white solids and satisfactory elemental analyses obtained for a representative selection. Some of the cationic complexes are unstable and could be identified only by means of their ^{31}P NMR spectra (see section 2.2.2). The mass spectra of the isolated complexes generally show the expected parent ion, $[M]^+$, or, less frequently, [M – ligand]$^+$, as the highest peak, corresponding to the fragment $[Pt(C_6H_3$-5-Me-2-$PPh_2)(PPh_2$-4-tol$)]^+$, and the IR spectra



L = O-donors: THF (**17**), Ph_3PO (**18**)
N-donors: NH_3 (**19**),[c] NEt_3 (**20**),[c] $PhNH_2$ (**21**),[c] $RC_6H_4NH_2$[c] [R = *o*-Me (**22**), *m*-Me (**23**), *p*-Me (**24**)], C_5H_5N (**25**),[c] NCMe (**26**)
S/Se-donors: SMe_2 (**27**), SEt_2 (**28**), SPh_2 (**29**), THT (**30**), DMSO (**31**), Ph_3PS (**32**), Ph_3PSe (**33**)
P/As/Sb-donors: PPh_2-4-tol (**34**), $AsPh_3$ (**35**), $SbPh_3$ (**36**), $P(OPh)_3$ (**37**), $P(OMe)_3$ (**38**)
C-donors: CO (**39**), *t*BuNC (**40**),[c] MeC≡CMe (**41**), PhC≡CPh (**42**)

[a] Ag_2O/H_2O. [b] $AgBF_4$/THF, then $NaNO_2$. [c] $AgBF_4$/THF, then L.

Scheme 2.

of the neutral complexes contain the usual *ortho*-metallation bands at ca. 1570 and 725 cm^{-1}. The ^{31}P NMR spectra generally consist of a pair of doublets with ^{195}Pt satellites, that due to PPh$_2$-4-tol being in the region of $\delta \approx 20$ ppm with J(Pt-P) ≈ 2000 Hz. The second doublet, due to the phosphorus atom in the four-membered ring, varies markedly in both chemical shift (δ = –50.7 to –86.5 ppm) and in J(Pt-P) (1122–3835 Hz), depending on the nature of the introduced ligand. The small doublet coupling (5–10 Hz) is as expected for inequivalent *cis*-phosphorus nuclei in platinum(II) complexes. The observed pattern in the ^{31}P NMR spectra becomes more complex for complexes in which the introduced ligand is a tertiary phosphane, phosphane chalcogenide or phosphite ligand (see below). We now discuss individual members of the series in more detail, and, unless specified otherwise, compound numbers refer to the *cis*-isomer.

2.2.1 Neutral Complexes cis-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (X = F, OH, OCOMe, OCOPh, N_3, NCO, NCS, NCSe, NO_2)

The fluoro complex *cis*-[PtF(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (**7**) was obtained in good yield by treatment of **2** in CH$_2$Cl$_2$ with AgF in the absence of light over a period of 3 d. In the ^{31}P NMR spectrum, the pair of doublets due to the inequivalent phosphorus nuclei are further split by coupling with ^{19}F (I = 1/2, 100%) [^2J(P-F) = 26.1 Hz (*cis*) and 161.5 Hz (*trans*)]. The ^{19}F NMR spectrum shows a doublet of doublets centred at δ = –285.1 ppm, arising from coupling with two inequivalent phosphorus nuclei, together with ^{195}Pt satellites [J(Pt-F) = 241 Hz], these data being consistent with the presence of a covalent Pt–F bond.[34–36] The Pt-F and Pt-P couplings are reproduced in the ^{195}Pt NMR spectrum, which consists of a doublet of double doublets centred at δ = –4243 ppm (relative to aqueous Na$_2$PtCl$_6$) [J(Pt-F) = 235 Hz, J(Pt-P) = 1999, 3376 Hz].

In comparison with the plethora of platinum complexes with chloride, bromide and iodide, those with fluoride are fairly rare and have only recently received attention.[37–39] It has usually been assumed, on the basis of the Class A character of fluoride ion and the Class B character of platinum, that Pt–F bonds will be relatively weak, and only a limited number of preparative methods have been developed. Moreover, the tendency of F$^-$ to form hydrogen bonds with water and other protic molecules can result in the isolation of complexes containing coordinated OH$^-$, H$_2$O or HF$_2^-$. Nevertheless, a number of Pt–F complexes containing "soft" co-ligands have been characterised structurally, e.g., *cis*-[PtF{CH(CF$_3$)$_2$}(PPh$_3$)$_2$],[40] [PtF(PEt$_3$)$_3$]BF$_4$,[41] [PtF(CH$_3$)$_3$]$_4$,[42] and *trans*-[PtF(Ph)(PPh$_3$)$_2$].[43]

Treatment of a solution of **2** with an excess of moist Ag$_2$O in the dark for 3 d gave the hydroxido complex, *cis*-[Pt(OH)(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (**8**) contaminated with ca. 5% of the starting material. Attempts to force the reaction to completion by extending the reaction time, or by sonication, caused extensive decomposition. Likewise, the attempted reactions of **2** or the derived THF cation *cis*-[Pt(THF)(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)]$^+$ (**17**) (see below) with NaOH were unsuccessful, although these procedures have worked well for many other hydroxido organoplatinum(II) complexes containing tertiary phosphanes.[9,44,45] The silver oxide procedure has been used to prepare functionalised σ-alkyl complexes of platinum(II) from *cis*-[PtCl$_2$(PEt$_3$)$_2$][46] and *trans*-[PtXRL$_2$] (X = I, R = Me, L = PPh$_3$; X = Cl, R = Ph, L = PMe$_2$Ph, PEt$_3$)[44] in the presence of acidic hydrocarbons such as acetone and nitromethane. The ^{1}H NMR spectrum of complex **8** shows a broad peak assigned to OH at δ = 1.25 ppm, together with the expected aromatic methyl resonances at δ = 2.30 and 2.33 ppm, and aromatic multiplets at δ = 6.8–8.2 ppm. The ES mass spectrum contains a peak at *m*/*z* = 763, corresponding to the [M – H]$^+$ fragment. Weak bands at 3657 and 1027 cm^{-1} in the IR spectrum are tentatively assigned to O–H stretching and Pt–OH bending vibrations, respectively.[47]

The acetato and benzoato complexes, **9** and **10**, respectively, were readily prepared by treatment of **2** with the appropriate silver salt. Unlike the corresponding trifluoroacetate, they cannot be prepared by treatment of **1** with the appropriate acids; evidently, acetic and benzoic acids are too weak to cleave the Pt–C σ-bonds. The IR spectra of complexes **9** and **10** show bands at ca. 1600 and 1300 cm^{-1} due to symmetric and asymmetric ν(COO) vibrations; the separations ($\Delta\tilde{\nu}$) are typical of κ^1-OCOR,[30,48,49] as found also in *cis*- and *trans*-**6**. The cyanido complex *cis*-[Pt(CN)(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (**11**) is also obtained in a similar way, i.e., by treatment of **2** with AgCN. It shows a typical ν(CN) band in its IR spectrum at 2128 cm^{-1}. The structure has been confirmed by X-ray crystallography (see below). An attempt to prepare a formato analogue of **9** and **10** by addition of sodium formate to a solution of **17** that had been generated in situ from **2**, led to rapid deposition of Pt metal (see below).

The complexes containing the pseudohalides azide, cyanate, thiocyanate and selenocyanate were prepared by treating a CH$_2$Cl$_2$ solution of **2** with a methanol solution of the appropriate alkali metal salt. The ^{31}P NMR spectrum of the azido complex **12** showed the expected pair of doublets, and the IR spectrum showed a strong band at 2043 cm^{-1} due to ν(N≡N).[50] The ^{31}P NMR spectrum of the cyanato complex **13** shows a broad, unresolved peak with ^{195}Pt satellites for the phosphorus atom *trans* to NCO; the broadening may be caused by scalar coupling of ^{31}P with the quadrupolar ^{14}N nucleus.[51,52] The IR spectrum of **13** contains a strong ν(CN) band at 2214 cm^{-1}, which is in the region usually observed for *N*-bonded NCO complexes,[53] but there was also a shoulder at 2170 cm^{-1}. We did not establish whether this is due to the formation of some KNCO in the KBr disc or to a solid-state splitting; it seems unlikely that some *O*-bonded isomer is present in the isolated solid.

The IR spectrum of the thiocyanato complex *cis*-[Pt(CNS)(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (**14**) shows only one ν(CN) band at 2212 cm^{-1} in CHCl$_3$ but two bands at 2212 and 2093 cm^{-1} in a KBr disc, which are probably due to *S*- and *N*-linkage isomers. We were unable to confirm this explanation by assigning bands due to ν(M–NCS), ν(CS) or δ(NCS)[54] because of interfering ligand absorption, but the assumption is supported by the ^{31}P NMR spectrum, which shows two pairs of doublets of approximately equal intensity, at δ = 18.8 and –68.2, and at 16.7 and –80.0 ppm. The latter pair is assigned to the *N*CS isomer on the basis of the observed broadness of the peak at δ = –80.0 ppm, which presumably arises from interaction with the ^{14}N quadrupole; this peak sharpens as the temperature is lowered, as observed in related systems.[52]

The selenocyanato complex *cis*-[Pt(CNSe)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (**15**) could not be isolated in a pure state because of its ready decomposition to the cyanido complex **11**, among other unidentified products. The ^{31}P NMR spectrum of **15** shows a pair of sharp doublets at δ = 19.2 and –68.8 ppm, the latter displaying an additional coupling of 82.2 Hz that is typical of $^2J(^{77}Se\text{-}^{31}P)$;[55,56] this observation is consistent with the presence of *Se*CN. Thus, for the three complexes containing XCN as ligands, only the *N*-bound species is present when X = O, only the X-bound species is present when X = Se, and both isomers are formed when X = S. The trend is consistent with expectations based on the hard/soft acid/base theory.

The nitro complex *cis*-[Pt(NO_2)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (**16**) was obtained almost quantitatively as an off-white solid by reaction of $NaNO_2$ with a solution of **17**. Its IR spectrum shows three strong bands at 1384, 1331 and 817 cm^{-1} corresponding to the asymmetric ν(NO_2), symmetric ν(NO_2) and δ(ONO) vibrations, respectively. The separation between the first two bands is typical of κ-*N*O_2 complexes and is much less than that of κ-*O*NO (nitrite) complexes, which generally shows bands at ca. 1450 and 1100 cm^{-1} in their IR spectra.[57] Similar bands for κ-*N*O_2 have been observed in the complexes [Pt(NO_2)$_2$(*cis*-Ph_2PCH=$CHPPh_2$)][58] and [Pt(en)$_2$(μ-C_5H_4NO)$_2$(NO_2)(NO_3)][NO_3]$_2$ (C_5H_4NO = α-pyridonato),[59] and the mode of coordination has been confirmed by X-ray crystallography in the latter.

2.2.2 Salts *cis-[PtL(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)]BF_4 (L = Various Neutral Ligands)*

As mentioned in section 2.2, these salts are obtained by abstraction of Cl^- from **2** with $AgBF_4$ in the presence of L, as shown in Scheme 2. Those having L = Ph_3PO (**18**), NH_3 (**19**), NEt_3 (**20**), aromatic amines (**21**–**24**), pyridine (**25**), SMe_2 (**27**), Ph_3PS (**32**), Ph_3PSe (**33**), PPh_2-4-tol (**34**), $AsPh_3$ (**35**), $SbPh_3$ (**36**) and P(OPh)$_3$ (**37**) were isolated, usually as colourless or off-white solids; exceptionally, those derived from *o*-, *m*- and *p*-toluidine were obtained as red or purple solids, probably owing to the formation of organic oxidation products in the presence of traces of the Ag^+ oxidant. The THF and MeCN salts, **17** and **26**, could not be isolated; both isomerised rapidly to the corresponding *trans*-isomers. The salts containing L = SEt_2 (**28**), SPh_2 (**29**), CO (**39**), MeC≡CMe (**41**) and PhC≡CPh (**42**) are also unstable and were identified only by their ^{31}P NMR spectra, measured on solutions prepared in situ.

The ^1H NMR spectrum of the SMe_2 complex **27** shows the aromatic multiplets and two aromatic methyl resonances arising from the inequivalent phosphane ligands. The methyl protons of SMe_2 appear as two singlets flanked by broad ^{195}Pt satellites [^3J(Pt-H) = 40.6 Hz]; we have not investigated whether this is caused by inequivalence of the methyl groups or coupling with ^{31}P. The ammonia complex **19** also shows the expected aromatic and methyl resonances in its ^1H NMR spectrum, together with a broad peak at δ = 3.42 ppm with ^{195}Pt satellites [^2J(Pt-H) ≈ 30 Hz] assigned to coordinated NH_3. The ^1H NMR spectrum of the pyridine complex **25** contains peaks at δ = 7.93 [t, *J*(H-H) = 7.7 Hz], 8.39 [m with br. ^{195}Pt satellites, *J*(Pt-H) ≈ 15 Hz], and 8.75 [dd, *J*(H-H) = 1.5, 6.3 Hz] ppm due to the coordinated pyridine ligand, these signals being shifted significantly from those of the free ligand.

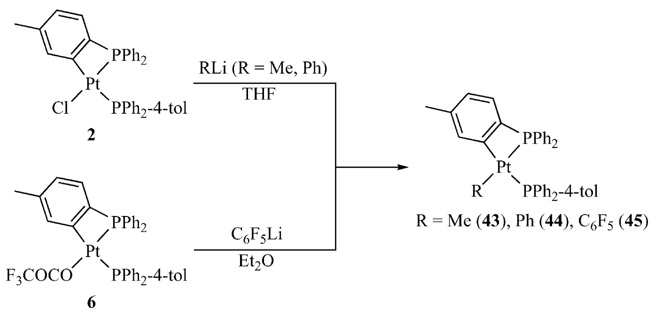
The ^1H NMR spectrum of *cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)$_2$]$^+$ (**34**) shows the expected three aromatic methyl singlets, and correspondingly, the ^{31}P NMR spectrum contains three doublets of doublets, with ^{195}Pt satellites, at δ = 23.0, 16.7 and –67.8 ppm due to the inequivalent PPh_2-4-tol ligands and an *ortho*-metallated PPh_2-4-tol group. The resonances at δ = –67.8 and 23.0 ppm display a coupling of 368 Hz, showing that the phosphorus atoms responsible for these signals are mutually *trans*.[32] All the Pt-P couplings (2845, 2004 and 2132 Hz) are reproduced in the ^{195}Pt NMR spectrum. The ^{31}P NMR spectroscopic data are very similar to those reported for [Pt(κ^2-2-$C_6H_4PPh_2$)(PPh_3)$_2$]$^+$.[60] The structure of **34**, as its BF_4 salt, has been confirmed by X-ray crystallography (see below).

The ^{31}P NMR spectra of the P(OPh)$_3$ and P(OMe)$_3$ complexes, **37** and **38** respectively, also show three well-separated doublets of doublets, with ^{195}Pt satellites, at δ ≈ 100, 20 and –70 ppm, the first and last being due to the phosphite and the *ortho*-metallated phosphane, respectively, and with a P-P coupling of about 600 Hz.

2.2.3 *η^1-Organyl Complexes cis-[PtR(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (R = Me, Ph, C_6F_5)*

The chlorido complex **2** in THF reacts with methyllithium and phenyllithium to give the corresponding η^1-C-bonded complexes *cis*-[PtR(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [R = Me (**43**), Ph (**44**)] as colourless solids in 70–80% yield (Scheme 3). Their ^1H NMR spectra show two aromatic methyl resonances in the region δ = 2.3–2.4 ppm, and the spectrum of **42** also shows a triplet due to Pt–CH_3 at δ = 0.93 [*J*(P-H) = 7.1 Hz] ppm flanked by ^{195}Pt satellites [*J*(Pt-H) = 74.7 Hz]. Similar spectral parameters for the Pt–CH_3 resonances have been reported for *cis*-dimethylplatinum(II) complexes $PtMe_2L_2$ containing either monodentate tertiary phosphanes (L)[61] or bidentate ditertiary phosphanes (L_2).[62]

Surprisingly, complex **2** failed to react with C_6F_5Li in diethyl ether, but the corresponding reaction with the trifluoroacetato complex **6** gave *cis*-[Pt(C_6F_5)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (**45**) as a colourless solid in ca. 80% yield. In contrast with **43** and **44**, whose ^{31}P NMR spectra consist of the usual pair of doublets, the shielded resonance



Scheme 3.

due to the phosphorus atom in the four-membered ring of **45** appears as an octet because of its coupling to ^{19}F nuclei of the *trans*-C_6F_5 group; the resonance due to the phosphorus atom of PPh_2-4-tol that is *cis* to the C_6F_5 group shows no such coupling and appears as the usual doublet. Similar effects have been observed for the phosphorus atom *trans* to the C_6F_5 group in, for example, *cis*-[Pt(OCHO)(C_6F_5)(PPh_3)$_2$][63] and [M(C_6F_5)(SC_6F_5)(dppe)] (M = Pd, Pt).[64] The ^{19}F NMR spectrum of **45** contains three multiplets (due to F-F coupling) at δ_F = –116.4, –164.4 and –165.5 ppm assigned to the *ortho*-, *meta*- and *para*-fluorine atoms of C_6F_5, respectively; as observed in other Pt^{II}-C_6F_5 complexes, the first resonance shows coupling with ^{195}Pt [^3J(Pt-F) = 406 Hz]. The structures of complexes **43** and **45** have been determined by X-ray crystallography (see below).

Attempts to prepare a hydrido complex *cis*-[PtH(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] similar to **43**–**45** by treating either **2** or **6** with $NaBH_4$ failed; reduction to metallic platinum was observed.

2.3 Molcular Structures of *trans*-[Pt(κ^1-$OOCCF_3$)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (*trans*-6), *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = Cl (2), C_6F_5 (45), CN (11), Me (43)] and *cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)$_2$] BF_4 (34)

These have been determined by single-crystal X-ray crystallography and are shown, together with selected metrical data, in Figures 1, 2, and 3 and S1–S3, respectively. All the complexes show marked angular distortions from the expected square-planar geometry about the metal centre owing to the narrow bite angle (ca. 69°) of κ^2-C_6H_3-5-Me-2-PPh_2, this value being typical of chelate ligands of the 2-$C_6H_4PR_2$ type.[65] Thus, in *trans*-**6**, the P–Pt–P unit deviates by 15° from linearity, and the angle P(1)–Pt(1)–O(1) opens to 105° from the expected value of 90° [P(1) is the phosphorus atom in the chelate ring]. In complexes **2**, **11**, **43**, and **45**, the angle subtended at the metal atom by the mutually *cis*-phosphorus atoms is ca. 106°, probably as a consequence of steric repulsion between the bulky ligand systems, and the angle P(1)–Pt(1)–X, where X is the formally *trans*-ligand atom, is only ca. 160°. In the same series, the Pt–P bond lengths in the chelate ring are 2.2539(8) Å (**2**), 2.3169(8) Å (**11**), 2.3174(6) Å (**45**) and 2.3324(7) Å (**43**), which would correspond to a *trans*-influence order Cl < CN ≈ C_6F_5 < Me; the Pt–C distances in the chelate ring remain equal, within experimental error, at 2.06 Å. The Pt–P distances to PPh_2-4-tol show a less marked trend in the opposite direction, namely, 2.2903(7) Å (**43**), 2.3129(6) Å (**45**), 2.3225(8) Å (**11**) and 2.3350(8) Å (**2**).

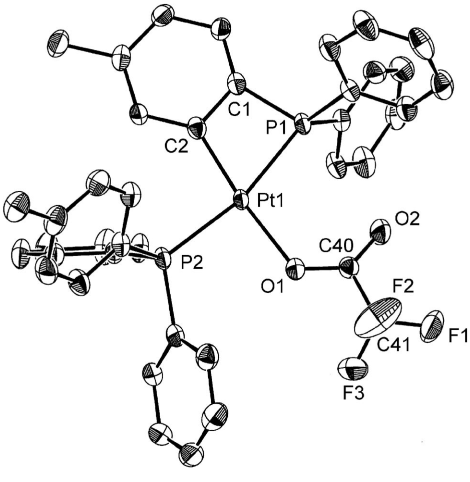


Figure 1. Molecular structure of *trans*-[Pt(κ^1-$OCOCF_3$)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (*trans*-**6**). Ellipsoids show 30% probability levels, and hydrogen atoms have been deleted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–P(1) 2.3153(8), Pt(1)–P(2) 2.2931(8), Pt(1)–C(2) 2.002(4), Pt(1)–O(1) 2.118(2); P(1)–Pt(1)–P(2) 165.30(3), P(2)–Pt(1)–O(1) 89.46(7), O(1)–Pt(1)–C(2) 173.66(11), C(2)–Pt(1)–P(1) 69.2(1), P(1)–Pt(1)–O(1) 105.09(7), P(2)–Pt(1)–C(2) 96.4(1).

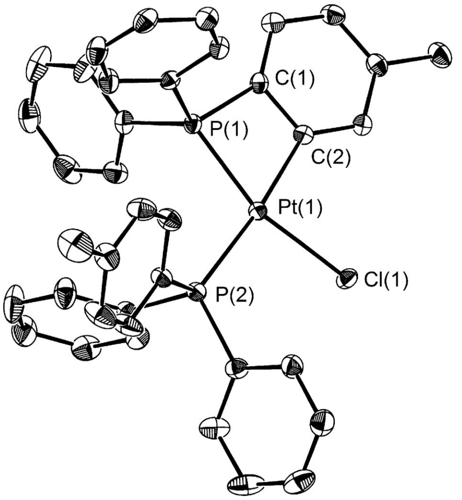


Figure 2. Molecular structure of *cis*-[PtCl(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (**2**). Ellipsoids show 30% probability levels, and hydrogen atoms have been deleted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–P(1) 2.2539(8), Pt(1)–P(2) 2.3350(8), Pt(1)–C(2) 2.056(3), Pt(1)–Cl(1) 2.3560(7); P(1)–Pt(1)–P(2) 105.78(3), P(2)–Pt(1)–Cl(1) 93.57(3), Cl(1)–Pt(1)–C(2) 91.81(9), C(2)–Pt(1)–P(1) 68.78(9), P(1)–Pt(1)–Cl(1) 160.45(3), P(2)–Pt(1)–C(2) 174.42(9).

In complex **2**, the Pt–Cl bond length of 2.3560(7) Å is similar to those observed in other platinum(II) complexes in which Cl is *trans* to PR_3, e.g., 2.348(15) Å in *cis*-[$PtCl_2$(PPh_3)$_2$],[66] 2.355 and 2.341 Å in [$PtCl_2$(dppe)],[67] and 2.367(3) Å in *cis*-[$PtCl_2$(SMe_2)(PMe_2Ph)].[68] The Pt–

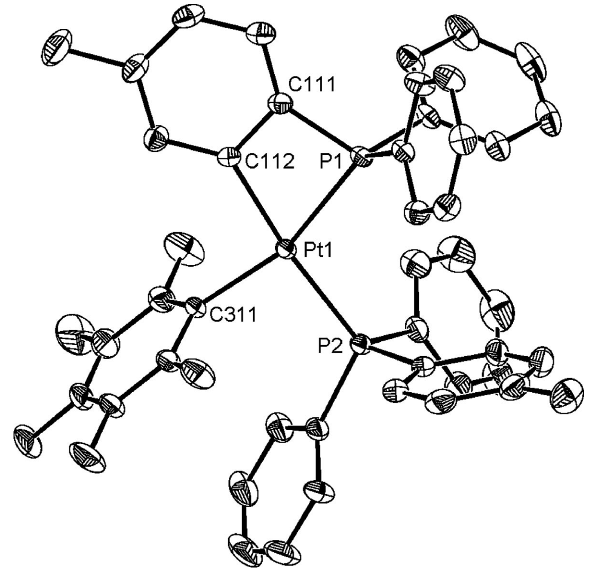


Figure 3. Molecular structure of *cis*-[Pt(C_6F_5)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (**45**). Ellipsoids show 30% probability levels, and hydrogen atoms have been deleted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–P(1) 2.3174(6), Pt(1)–P(2) 2.3129(6), Pt(1)–C(112) 2.051(2), Pt(1)–C(311) 2.061(2); P(1)–Pt(1)–P(2) 105.87(2), P(2)–Pt(1)–C(311) 91.53(7), C(311)–Pt(1)–C(112) 94.21(9), C(112)–Pt(1)–P(1) 68.38(6), P(1)–Pt(1)–C(311) 162.59(7), P(2)–Pt(1)–C(112) 173.56(6).

CN bond length of 1.999(4) Å in complex **11** is comparable with the values of 2.018(5) and 2.002(5) Å observed in [Pt$(CN)_2$(*cis*-dppen)].[69]

The Pt–CH_3 distance in **43** [2.089(3) Å] is similar to those found in [PtMe(*n*-C_3F_7)(dppe)] [2.109(7) Å][70] and [$PtMe_2$(dppf)] [2.094(3), 2.102(4) Å],[62] and the Pt–C_6F_5 distance in **45** [2.061(2) Å] is comparable with those found in many Pt^{II}-C_6F_5 complexes, e.g., [Pt$(C_6F_5)_2$(dppb)] [2.065(8) Å][71] and [Pt$(C_6F_5)_2$($Ph_2CHIPPh_2$)] [2.067(5) Å].[72] An almost identical distance [2.052(7) Å] was found for the Pt–Ph bond in the similar non-fluorinated compound [PtPh(κ^2-2-$C_6H_4PPh_2$)(PPh_3)].[73]

The X-ray structure of *trans*-**6** confirms the presence of monodentate trifluoroacetate, the Pt–O distance being 2.118(2) Å. The Pt–C distance in the four-membered chelate ring [2.002(4) Å] is significantly shorter than those in **2**, **11**, **43** and **45**, reflecting the low *trans*-influence of trifluoroacetate.

In **34**, the bond length of 2.3361(11) Å for Pt(1)–P(2) *trans* to the phosphorus atom in the chelate ring is only slightly larger than that for phosphorus atom P(3) *trans* to the metallated aryl ring [2.3294(11) Å], suggesting that the *trans*-influences of the arylphosphane and aryl groups are comparable. However, the Pt–P bond length in the chelate ring of **34** and in the non-methylated analogue [Pt(κ^2-2-$C_6H_4PPh_2$)$(PPh_3)_2$]SbF_6[60] differ significantly [2.3095(11) Å in **34**, 2.3126(11) Å in the non-methylated analogue], as also do the Pt–P bond lengths *trans* to the phosphorus atom in the chelate ring [2.3361(11), 2.3079(13) Å, respectively]. The P–Pt–P (*trans*) angle in both structures deviates markedly from linearity (163° and 158.5°, respectively), as observed also in **2**, **11**, **43** and **45**. There are also small but significant differences (3–4°) in many of the bond angles about the platinum atom in **34** and in [Pt(κ^2-2-$C_6H_4PPh_2$)$(PPh_3)_2$]SbF_6, which presumably are caused by lattice effects (different space groups, different anions). This emphasises the caution to be exercised in interpreting small changes in metrical data determined in the solid state, especially for ionic compounds.

2.4 ^{31}P NMR Spectra and the *trans*-Influence Series

The ^{31}P NMR spectroscopic data for *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] and *cis*-[PtL(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)]$^+$ (X = anionic ligand; L = neutral ligand) are collected in Table 1. The data are listed in order of decreasing values of J(Pt-P_B), P_A and P_B being the phosphorus atoms of PPh_2-4-tol and the four-membered chelate ring, respectively. The ^{31}P chemical shifts of P_A and P_B fall within fairly narrow ranges (δ = 14–24 and –65 to –87 ppm, respectively), the only exceptions being the $\delta(P_B)$ values of ca. –50 ppm for X = Me (**43**) and Ph (**44**). The magnitude of J(Pt-P_A) also spans a fairly narrow range (1930–2100 Hz), whereas J(Pt-P_B) varies over a much wider range (1040–3800 Hz) as X and L are varied, reflecting, at least to a first approximation, changes in the electronic nature of X and L (see Introduction). Similar behaviour was observed in the series based on [PtR(dppe)] (R = Me, Ph, 1-cyclohexenyl).[9] As in that series, there is no obvious correlation between $\delta(P_B)$ and J(Pt-P_B).

The listing of ligands in Table 1 gives the order of increasing *trans*-influence [decreasing J(Pt-P)]. While there are some obvious exceptions and considerable overlap between the ranges, the general trend of increasing *trans*-influence with decreasing electronegativity of the donor atom [$O < N \approx S < Se < As < P < \sigma$-C] is followed. It has been pointed out[4] that derived *trans*-influence series depend both on the type of complexes and on the physical property studied. This remains true even when NMR coupling constants form the basis of comparison. For example, one series of increasing *trans*-influence based on ^1J(Pt-P) for a range of platinum(II) complexes, is $NO_3^- < I^- \approx Br^- \approx Cl^- < NCS^- \approx NCO^- \approx N_3^- \approx C_5H_5N <$ *p*-toluidine $< NO_2^- < CN^- \approx P(OPh)_3 < Me^- < Ph^-$,[8] which differs from the series in Table 1 in its lower placement of iodide ion and pyridine. For a series based on ^2J(Pt-CH_3), the order is $NO_3^- < Br^- \approx Cl^- \approx I^- < N_3^- \approx NCS^- \approx NCO^- < MeC{\equiv}CMe < C_5H_5N < NO_2^- < AsPh_3 < CO < CN^- < P(OPh)_3 < SbPh_3$,[5] which also differs significantly from that in Table 1. In general, however, there is a reasonable linear correlation between the J(Pt-P) values obtained in the present work and those derived from studies of [PtMeX(dppe)] and [PtMeL(dppe)]$^+$ complexes,[9,71,74] as shown in Figure 4. This is not surprising given the similarity of the nature and disposition of the donor sets, and it suggests that the marked distortion from strictly planar geometry of the 5-Me-2-$C_6H_3PPh_2$ complexes is unlikely to affect seriously the derived *trans*-influence series. The J(Pt-

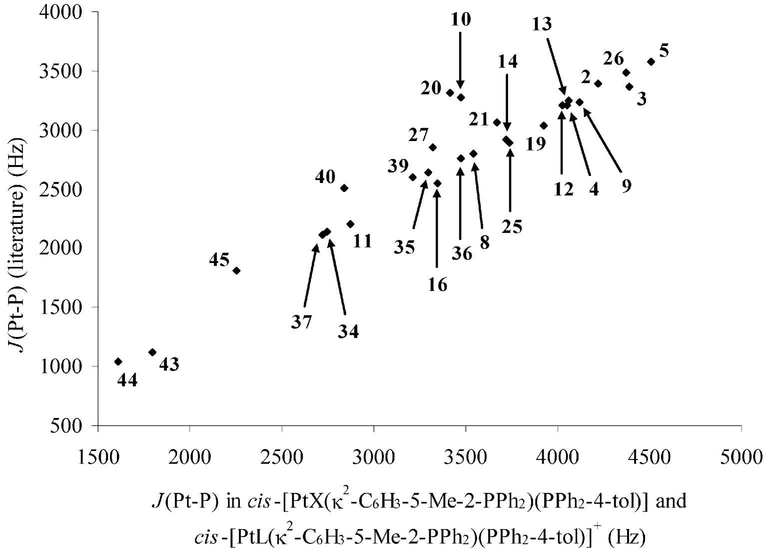


Figure 4. Plot of J(Pt-P) [Hz] for *cis*-[PtMeX(dppe)] and *cis*-[PtMeL(dppe)]$^+$ vs. J(Pt-P) [Hz] for *cis*-[PtX(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] and *cis*-[PtL(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)]$^+$ (X = anionic ligand, L = neutral ligand). Values of J(Pt-P) for the dppe complexes are taken from ref.[9], except those for X = C$_6$F$_5$ (ref.[71]) and L = NH$_3$ (ref.[74]). Values for X = Br and OCOPh have been omitted for clarity. For other comments, see text.

P) values for the dppe complexes, for a given ligand, are generally 600–1000 Hz larger than for the corresponding *ortho*-platinated complexes, probably as a consequence of the four-membered ring in the latter. Since J(Pt-P) values for X = Br, NCS and for L = NEt$_3$, PhNH$_2$, SMe$_2$ and *t*BuNC were unavailable in the PtMe(dppe) series, we used for comparison in Figure 4 the corresponding J(Pt-P) values from *cis*-[PtX(*n*Bu)(PEt$_3$)$_2$] (X = Br, NCS),[75] *trans*-[PtCl$_2$(L)(PMe$_2$Ph)] (L = NEt$_3$, PhNH$_2$),[76] *trans*-[PtCl$_2$(SMe$_2$)(PCy$_3$)][77] and *trans*-[PtCl$_2$(CN^{t}Bu)(PCy$_3$)].[77] Despite the obvious errors thereby introduced resulting from different *cis*-ligands and different tertiary phosphanes, the only marked discrepancy occurs for L = NEt$_3$.[20] The plot omits points corresponding to SeCN$^-$, Ph$_3$PO, Ph$_3$PS, SEt$_2$, SPh$_2$, toluidine (*o*-, *m*- and *p*-), THT, THF, DMSO, MeC≡CMe and PhC≡CPh, for which literature J(Pt-P) data could not be found.

Table 2 shows a comparison of Pt-P coupling constants and Pt–P bond lengths for the *ortho*-platinated complexes whose structures have been determined in this work. It is clear that the shortest Pt–P distances in the chelate ring occurs for complex **2** (X = Cl), which has one of the highest values of J(Pt-P). Conversely, the longest Pt–P distance is found in complex **43** (X = Me), which has one of the lowest J(Pt-P) values. Moreover, the position of C$_6$F$_5^-$ in the *trans*-influence series above Cl$^-$ and below Me$^-$ is reflected in both the Pt–P bond length and J(Pt-P) data. The data also agree in the placement of CN$^-$ above Cl$^-$ and below Me$^-$ in the *trans*-influence series. However, the correspondence between J(Pt-P) and Pt–P bond length data is not exact, since the Pt–P bond lengths for X = CN (**11**) and X = C$_6$F$_5$ (**45**) are equal, within experimental error, whereas the J(Pt-P) value for **11** is ca. 400 Hz higher than for **45**. The placement of PPh$_3$ or PPh$_2$-4-tol is problematic because of the significantly different Pt–P bond lengths in the chelate ring of complex **34** and in its close relative [Pt(κ^2-2-C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]SbF$_6$ (see above), even though the J(Pt-P) values are almost identical. Neither of the reported Pt–P bond lengths fits well with the trend in J(Pt-P). Probably the range of Pt–P bond lengths is too small to allow meaningful conclusions except for ligands at the extremes of the *trans*-influence series.

Table 2. Pt–P bond lengths [Å] and coupling constants [Hz] for neutral *cis*-[PtX(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] complexes and *cis*-[PtL(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)]BF$_4$ salts.

X or L	*trans* to X or L		*cis* to X or L	
	d(Pt–P)	*J*(Pt-P)	*d*(Pt–P)	*J*(Pt-P)
Cl (**2**)	2.2539(8)	3392	2.3350(8)	1990
CN (**11**)	2.3169(8)	2207	2.3225(8)	1888
PPh$_2$-4-tol (**34**)	2.3095(11)	2132	2.3294(11)	2004
PPh$_3$[a]	2.3126(13)	2135	2.3229(12)	2008
C$_6$F$_5$ (**45**)	2.3174(6)	1803	2.3129(6)	1981
Me (**43**)	2.3324(7)	1122	2.2903(7)	2123

[a] Data for [Pt(κ^2-2-C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]SbF$_6$ from ref.[60]

Table 2 also shows that the Pt–P distances to the spectator PPh$_2$-4-tol ligand (P$_A$) that is *cis* to X or L tend to decrease as the Pt–P distances *trans* to X or L increase; again, the trend is clearest at the extremes. Except for X = Cl (**2**) and Me (**43**), no corresponding trend in Pt-P coupling constants is discernible. The bond-length trend is consistent with earlier evidence for a poorly understood *cis*-influence that is somewhat weaker than, and operates in the opposite direction to, the *trans*-influence.[8,13,14,20,41,78–82]

We now consider some of the individual trends in the *trans*-influence series in more detail. Among the halides, the order Cl$^-$ < Br$^-$ < I$^-$ seems well established[5,6,83] and the apparently anomalous order Cl$^-$ < F$^-$ agrees with that derived from Pt-P coupling constants in [PtXL$_3$]$^+$ (L = PEt$_3$,

PMe_2Ph).[35] In contrast, the order $F^- < Cl^- < Br^- < I^-$ is derived from ν(Rh=C) values in planar rhodium(I) complexes [$RhXL(PiPr_3)_2$] (L = $C=CH_2$, CO).[84] This represents an example of the well-known dependence of the placement of a ligand in the *trans*-influence series on the physical method used to assess it.[5] Exceptionally, for the three heavier halides, there is a perfect linear correlation between $J(Pt-P_B)$ and $\delta(P_B)$, but fluoride is anomalous.

The *trans*-influences of the neutral O-donor ligands THF and Ph_3PO are the lowest of all the ligands studied and, in particular, are lower than those of the oxy anions, which presumably are more covalently bound to the platinum(II) atom. The order of the *J*(Pt-P) values for the oxy anions parallels that of the dissociation constants of the free acids. In agreement with earlier work,[9] the *J*(Pt-P) value for OH^- is considerably less than that for the oxy anions and places this ligand close to neutral sulfur donors and $SbPh_3$ in the *trans*-influence series.

Of the neutral N-donors examined, acetonitrile and triethylamine have the lowest *trans*-influences, though both are higher in the series than THF, because of the lower electronegativity of N. They are lower than ammonia, aniline and *o*-toluidine, which do not differ greatly. *p*-Toluidine comes above the other aromatic amines, possibly indicative of stronger σ-donation and greater covalency in the Pt–N bond, and this effect is even more marked with pyridine.

The order of *trans*-influence of the triarylpnicogens obtained in this work, PPh_2-4-tol > $AsPh_3 \approx SbPh_3$, agrees well with the order $PPh_3 > AsPh_3 \approx SbPh_3$ obtained from the earlier ^{31}P NMR study of [PtMe(L)(dppe)]$^{+}$[9] and with the results of X-ray crystallographic studies, e.g., of *cis*-[$PtBr_2(SbPh_3)(PPh_3)$][15] and [$PtI_3(L)$]$^-$ (L = PPh_3, $AsPh_3$, $SbPh_3$).[3,4] Further, the conclusion from our work that $AsPh_3$ and *S*-DMSO have almost equal *trans*-influences, both being higher in the series than SMe_2, is supported by a comparison of the Pt–Cl distances in *cis*-[$PtCl_2(SMe_2)(L)$] (L = $AsPh_3$, DMSO).[17]

As noted above, C_6F_5 has a higher *trans*-influence than Cl, and this confirms the trend evident from both the Pt–P bond lengths and coupling constants in *cis*-[$PtCl(C_6F_5)$(dppe)].[71] The smaller *trans*-influence of C_6F_5 relative to that of C_6H_5 evident from our data also emerges from a comparison of the Pt-P coupling constants *trans* to the σ-carbon-bonded group in *cis*-[PtCl(R)(dppe)] [R = Ph (1613 Hz);[9] R = C_6F_5 (2251 Hz)[71]], although it should be noted that the Pt-P coupling constants *trans* to Cl also differ substantially in the opposite sense in these two compounds (4165 Hz, 3720 Hz, respectively). The reduction of *trans*-influence, as assessed by ^{31}P NMR spectroscopy, caused by complete replacement of all the hydrogen atoms of C_6H_5 by fluorine is similar to, though somewhat larger than, that observed in going from CH_3 to CF_3.[9]

Finally, according to the *J*(Pt-P) data, the alkynes RC≡CR (R = Me, Ph) have relatively low *trans*-influences, being slightly above Cl^- and in about the same position as NCO^- in the series, in agreement with conclusions based on $^1J(Pt-CH_3)$ and $^2J(Pt-CH_3)$ data for ligands attached to the fragment *trans*-[$PtMe(PMe_2Ph)_2$].[85,86]

3. Conclusions

We have determined the Pt-P coupling constants for a series of neutral and cationic chelate complexes, *cis*-[$PtX(\kappa^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)$] and *cis*-[$PtL(\kappa^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)$]$BF_4$. The *J*(Pt-P) values for the phosphorus atom in the four-membered ring can be ordered to provide an extensive *trans*-influence series that is in fair agreement with those derived previously from measurements of coupling constants of ^1H, ^{13}C or ^{31}P to ^{195}Pt in different series of complexes. For four of the neutral complexes there is a reasonable correlation between the *J*(Pt-P) values and the corresponding Pt–P bond lengths. The Pt–(PPh_2-4-tol) distances in the determined structures are also consistent with the existence of a *cis*-influence that runs opposite to the *trans*-influence.

4. Experimental Section

Abbreviations: DMSO = dimethyl sulfoxide; dppb = butane-1,4-diylbis(diphenylphosphane), dppe = ethane-1,2-diylbis(diphenylphosphane); dppen = ethene-1,2-diylbis(diphenylphosphane); dppf = ferrocene-1,1′-diylbis(diphenylphosphane); en = ethylenediamine; THF = tetrahydrofuran; THT = tetrahydrothiophene.

General Procedures: Experiments involving organolithium reagents were performed under dry argon with the use of standard Schlenk techniques. Diethyl ether, tetrahydrofuran, *n*-pentane and *n*-hexane were dried with sodium/benzophenone and toluene with sodium prior to use. IR spectra were measured as KBr discs or as hexachlorobutadiene or Nujol mulls between NaCl plates, and FIR spectra as polythene discs with a Perkin–Elmer Spectrum 2000 FT spectrometer. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were measured with a Varian Gemini 2000 spectrometer, and ^{19}F (188.2 MHz), ^{31}P (80.96 MHz) and ^{195}Pt (42.83 MHz) NMR spectra with a Varian XL-200E spectrometer. ^1H and ^{13}C NMR spectra are internally referenced to residual solvent signals, ^{19}F internally to $CFCl_3$, ^{31}P to external 85% H_3PO_4 and ^{195}Pt externally referenced to Na_2PtCl_6/D_2O. ^{31}P NMR spectroscopic data for the *cis*-complexes are listed in Table 1. Quoted multiplicities exclude ^{195}Pt satellites. Microanalyses were performed by the Microanalytical Unit at the Research School of Chemistry, Australian National University. Mass spectra were obtained with a VG ZAB-2SEQ spectrometer using NOPE as matrix (FAB), an HP 5970 MSD spectrometer (ES) or Bruker Biflex II spectrometer (MALDI). The complex [$Pt(\kappa^2-C_6H_3-5-Me-2-PPh_2)_2$] (**1**) was prepared as described previously.[21]

X-ray Crystallography: Data were collected at 200 K with a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and were measured by means of COLLECT.[87] Selected crystal data and details of data collection and structural refinement are in Table 3. The intensities of the reflections were measured, and the data were reduced by use of the programs Denzo and Scalepack.[88] The structures of complexes *trans*-**6**, **2**, **11**, and **43** were solved by heavy-atom Patterson methods (PATTY), expanded by standard Fourier synthesis (DIRDIF 92[89] for **2**, **11** and **43**, DIRDIF 96[90] for *trans*-**6**), and refined on *F* with use of TEXSAN[91] for **2**, **11**, **43**, or CRYSTALS[92] for *trans*-**6**. The structures of complexes **34** and **45** were solved by direct methods (SIR 92)[93] and refined on *F* with use of CRYSTALS.[92] Although the three aromatic rings of the PPh_2-4-tol ligand were clearly observed in the structures of *trans*-**6** and **45**, the 4-tolyl group and

Table 3. Crystal and structure refinement data for *trans*-[Pt(κ^1-OCOCF$_3$)(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (*trans*-**6**), *cis*-[PtX(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] [X = Cl (**2**), CN (**11**), CH$_3$ (**43**), C$_6$F$_5$ (**45**)] and *cis*-[Pt(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)$_2$]BF$_4$ (**34**).

	trans-**6**	**2**	**11**
Empirical formula	$C_{40}H_{33}F_3O_2P_2Pt\cdot0.5C_5H_{12}$	$C_{38}H_{33}ClP_2Pt\cdot0.5C_6H_6$	$C_{39}H_{33}NP_2Pt\cdot0.5C_6H_6$
Formula mass	895.81	821.23	811.79
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.6396(2)	11.0071(2)	11.1369(3)
b [Å]	10.8280(2)	12.6657(3)	12.6425(3)
c [Å]	17.4628(3)	13.5217(3)	13.5054(4)
α [°]	104.755(1)	72.114(1)	72.422(2)
β [°]	96.503(1)	75.622(1)	75.035(2)
γ [°]	100.138(1)	77.984(1)	77.359(2)
V [Å^3]	1888.50(6)	1719.91(7)	1730.67(9)
Z	2	2	2
Colour, habit	colourless, block	colourless, block	colourless, block
Crystal size [mm]	0.30 × 0.28 × 0.19	0.20 × 0.18 × 0.10	0.20 × 0.13 × 0.12
$\rho_{calcd.}$ [g cm^{-3}]	1.575	1.586	1.558
μ [mm^{-1}]	3.850	4.262	4.161
Total reflections	38531	44004	33574
Unique reflections	8648 (R_{int} = 0.040)	10039 (R_{int} = 0.043)	7977 (R_{int} = 0.037)
Used reflections	7029 [$I > 3\sigma(I)$]	8674 [$I > 2\sigma(I)$]	7240 [$I > 2\sigma(I)$]
Number of parameters	457	406	415
R (used reflections)	0.0261	0.0359	0.0302
Goodness of fit	1.0682	1.23	1.32
wR (used reflections)	0.0286	0.0355	0.0336
ρ_{max}, ρ_{min} [e Å^{-3}]	0.95, –1.06	0.38, –0.38	–1.06, –1.13
	34	**43**	**45**
Empirical formula	$C_{57}H_{50}BF_4P_3Pt\cdot CH_2Cl_2$	$C_{39}H_{36}P_2Pt\cdot0.5C_6H_6$	$C_{44}H_{33}F_5P_2Pt$
Formula mass	1194.77	800.81	913.77
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	19.1683(2)	11.1602(2)	14.5239(2)
b [Å]	15.2202(1)	12.6761(2)	12.5382(1)
c [Å]	20.3797(2)	13.4685(2)	20.6832(2)
α [°]	90	72.3105(7)	90
β [°]	117.5968(4)	76.1296(7)	90.6982(6)
γ [°]	90	77.1573(7)	90
V [Å^3]	5269.24(9)	1739.18(5)	3766.21(7)
Z	4	2	4
Colour, habit	colourless, plate	colourless, plate	colourless, block
Crystal size [mm]	0.32 × 0.20 × 0.05	0.25 × 0.19 × 0.12	0.43 × 0.28 × 0.15
$\rho_{calcd.}$ [g cm^{-3}]	1.506	1.529	1.611
μ [mm^{-1}]	2.896	4.138	3.866
Total reflections	128697	45235	69288
Unique reflections	15402 (R_{int} = 0.054)	10155 (R_{int} = 0.040)	8630 (R_{int} = 0.052)
Used reflections	7094 [$I > 3\sigma(I)$]	9331 [$I > 2\sigma(I)$]	6642 [$I > 3\sigma(I)$]
Number of parameters	651	406	479
R (used reflections)	0.0280	0.0305	0.0190
Goodness of fit	1.01	1.43	1.10
wR (used reflections)	0.0202	0.0353	0.0218
ρ_{max}, ρ_{min} [e Å^{-3}]	0.90, –0.60	0.87, –1.46	1.15, –1.03

one phenyl ring were disordered, as indicated by the presence of partly occupied methyl groups on C(23) and C(36) in *trans*-**6**, and on C(214) and C(224) in **45**. The relative occupancies of the methyl groups in both cases were refined. Similar behaviour was evident in the 4-tolyl groups of the ligand *trans* to P(1) in the structure of complex **34** and, in one case, the two images were sufficiently separated to allow modelling of each component and refinement of the relative populations, with restrains on distances, angles and planarity. Hydrogen atoms were generally included at idealised positions and ride on the atom to which they are bonded. Methyl groups were oriented to best-fit peaks observed in difference electron-density maps. CCDC-683243 (for **45**), -683244 (for **34**), -683245 (for *trans*-**6**), -683246 (for **2**), -683247 (for **11**), and -683248 (for **43**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparations

***cis*-[PtCl(κ^2-C$_6$H$_3$-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (2):** HCl (constant boiling aqueous solution, 98.8 µL, 0.548 mmol) in THF (4 mL) was added to a solution of **1** (409 mg, 0.548 mmol) in THF (10 mL). After the mixture had been stirred for 10 min, the solvent was removed in vacuo. The off-white solid was dissolved in toluene, and the solution was transferred to a silica gel column. The fraction that eluted with toluene was concentrated to ca. 1 mL volume, and *n*-hexane was added. The precipitated white solid was washed with *n*-hexane and dried in vacuo. The yield of **2** was 401 mg (93%).[1] ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, Me), 2.34 (s, 3 H, Me), 6.8–7.8 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –3944 [dd, *J*(Pt-P) = 1990, 3391 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2916 cm^{-1} (C–H str), 1569 (arom C=C str), 725 (C–H def) cm^{-1}. FIR (polythene): $\tilde{\nu}$ = 314 (Pt–Cl str) cm^{-1}. ES-MS: *m*/*z* = 782 [M]$^+$. $C_{38}H_{33}ClP_2Pt{\cdot}0.7C_6H_5CH_3$ (846.66): calcd. C 60.86, H 4.60, P 7.32; found C 60.87, H 4.60, P 7.79. The presence of toluene was confirmed by the observation of a singlet at δ = 2.35 ppm in the ^{1}H NMR spectrum. X-ray quality crystals were grown from benzene/*n*-pentane. Slow *cis* → *trans* isomerisation occurred when solutions of **2** were set aside. After 24 h, ca. 10% of *trans*-**2** was observed by ^{31}P NMR spectroscopy. Under CO, the isomerisation was quantitative after 30 min. ^{31}P NMR ($CDCl_3$): δ = 24.4 [d, *J*(P-P) = 447 Hz, *J*(Pt-P) = 3121 Hz], –61.8 [d, *J*(P-P) = 447 Hz, *J*(Pt-P) = 2196 Hz] ppm.

***cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = Br (3), ONO_2 (5), $OCOCF_3$ (6)]:** These were prepared similarly to **2** by treatment of **1** (409 mg, 0.548 mmol) with constant boiling HBr (93.7 µL), constant boiling HNO_3 (51 µL) or neat CF_3COOH (42 µL), respectively, and isolated as white solids in yields of 75–90%.

3: ^{1}H NMR ($CDCl_3$): δ = 1.53 (br. s, H_2O), 2.32 (s, 3 H, Me), 2.33 (s, 3 H, Me), 6.7–8.4 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –3787 [dd, *J*(Pt-P) = 1999, 3666 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (O–H str), 3051, 2919 (C–H str), 1570 (arom C=C str), 725 (C–H def) cm^{-1}. ES-MS: *m*/*z* = 827 [M]$^+$. $C_{38}H_{33}BrP_2Pt{\cdot}H_2O$ (844.63): calcd. C 54.04, H 4.18, P 7.33; found C 54.45, H 4.06, P 7.35.

5: ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.8–7.6 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –4108 [dd, *J*(Pt-P) = 2067, 3574 Hz] ppm. IR (hexachlorobutadiene): $\tilde{\nu}$ = 3052, 2918 (C–H str), 1480, 1435, 1272, 1098 [ν(ONO_2)] cm^{-1}. ES-MS: *m*/*z* = 746 [M – NO_3]$^+$. $C_{38}H_{33}NO_3P_2Pt{\cdot}0.3C_6H_5CH_3$ (836.35): calcd. C 57.71, H 4.28, N 1.67, P 7.38; found C 57.72, H 4.36, N 1.61, P 7.73. The presence of toluene was confirmed by the presence of a small peak at δ = 2.35 ppm in the ^{1}H NMR spectrum. When a solution of **5** in C_6D_6 was set aside for 24 h, the *trans*-isomer was formed quantitatively, as shown by ^{31}P NMR spectroscopy. ^{31}P NMR (C_6D_6): δ = 25.4 [d, *J*(P-P) = 428 Hz, *J*(Pt-P) = 3284 Hz], –52.6 [d, *J*(P-P) = 428 Hz, *J*(Pt-P) = 2337 Hz] ppm.

6: ^{1}H NMR ($CDCl_3$): δ = 2.20 (s, 3 H, Me), 2.22 (s, 3 H, Me), 6.6–7.9 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –4117 [dd, *J*(Pt-P) = 2037, 3507 Hz] ppm. IR (nujol): $\tilde{\nu}$ = 1699 cm^{-1} (C=O str), 1571 (arom C=C str) 1409, 1197 (C=O, C–O str), 1134, 1098 cm^{-1}. ES-MS: *m*/*z* = 859 [M]$^+$. $C_{40}H_{33}F_3O_2P_2Pt$ (859.72): calcd. C 55.88, H 3.87, P 7.21; found C 55.81, H 4.09, P 7.03. When a solution of **6** in C_6D_6 was set aside for 24 h, or stirred under CO for 30 min, the *trans*-isomer was formed quantitatively, as shown by ^{31}P NMR spectroscopy. ^{31}P NMR (C_6D_6): δ = 25.9 [d, *J*(P-P) = 441 Hz, *J*(Pt-P) = 3249 Hz], –52.7 [d, *J*(P-P) = 441 Hz, *J*(Pt-P) = 2361 Hz] ppm. X-ray quality crystals were obtained from benzene/*n*-pentane.

***cis*-[PtI(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (4):** A solution of **2** (100 mg, 0.128 mmol) in acetone (10 mL) was treated with NaI (57 mg, 0.380 mmol), and the mixture was stirred for 10 min. The solvent was removed in vacuo, and the residue was extracted with toluene. Chromatography on silica gel and workup as described for **2** gave complex **4** as a white solid (93 mg, 83%). ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, Me), 2.34 (s, 3 H, Me), 6.7–8.5 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –4064 [dd, *J*(Pt-P) = 2009, 3200 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2914 cm^{-1} (C–H str), 1568 (arom C=C str), 726 (C–H def) cm^{-1}. ES-MS: *m*/*z* = 875 [M]$^+$. $C_{38}H_{33}IP_2Pt{\cdot}0.5C_6H_5CH_3$ (919.68): calcd. C 54.20, H 4.06, P 6.74; found C 54.09, H 4.11, P 6.63. The presence of toluene was confirmed by the presence of a small singlet at δ = 2.35 ppm in the ^{1}H NMR spectrum.

***cis*-[Pt(κ*N*-N_3)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (12):** A solution of **2** (50 mg, 0.068 mmol) in CH_2Cl_2 (3 mL) was treated with NaN_3 (12 mg, 0.180 mmol) in methanol (3 mL), and the mixture was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with toluene (5 mL). The extract was filtered, and its volume was reduced to about half under reduced pressure. The white solid that precipitated on addition of *n*-pentane was re-dissolved in CH_2Cl_2 and re-precipitated with *n*-pentane. It was separated by filtration, washed with *n*-pentane, and dried in vacuo. The yield was 47 mg (94%). ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, Me), 2.35 (s, 3 H, Me), 6.8–8.2 (m, 27 H, arom) ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2918 cm^{-1} (C–H str), 2043 (N=N=N str), 1570 (arom C=C str), 725 (C–H def) cm^{-1}. FAB-MS: *m*/*z* (%) = 746 [M – N_3]$^+$. $C_{38}H_{33}N_3P_2Pt$ (788.73): calcd. C 57.87, H 4.22, N 5.33, P 7.85; found C 57.98, H 4.34, N 5.18, P 8.18.

***cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] [X = NCO (13), NCS/SCN (14), SeCN (15)]:** These were prepared similarly to **12** with use of NaOCN (12 mg, 0.180 mmol), NaSCN (15 mg, 0.180 mmol) and KSeCN (25 mg, 0.173 mmol), respectively. The complexes **13** and **14** were obtained almost quantitatively as white solids; complex **15** was obtained as a white solid (49 mg) containing about 25% of the desired product, 10% of the cyanido complex **11**, and other unidentified products of decomposition.

13: ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, Me), 2.34 (s, 3 H, Me), 6.8–7.8 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –3956 [dd, *J*(Pt-P) = 1940, 3232 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3050, 2917 cm^{-1} (C–H str), 2214, 2170 (C≡N str), 1570 (arom C=C str), 725 (C–H def) cm^{-1}. ES-MS: *m*/*z* = 787 [M]$^+$. $C_{39}H_{33}NOP_2Pt$ (788.72): calcd. C 59.39, H 4.22, N 1.78, P 7.85; found C 59.09, H 4.35, N 1.76, P 8.22.

14: 1:1 mixture of κ*N* and κ*S* isomers. ^{1}H NMR ($CDCl_3$): δ = 2.34 (br. s, 12 H, Me), 6.7–8.0 (m, 54 H, arom) ppm. ^{195}Pt{^{1}H} NMR ($CDCl_3$): δ = –3747 [dd, *J*(Pt-P) = 2037, 2953 Hz] ppm (κ*S*-SCN); –3801 [dd, *J*(Pt-P) = 2180, 3085 Hz] ppm (κ*N*-NCS). IR (KBr): $\tilde{\nu}$ = 3052, 2917 cm^{-1} (C–H str), 2212, 2093 (C=N str), 1570 (arom C=C str), 725 (C–H def) cm^{-1}. IR ($CHCl_3$): $\tilde{\nu}$ = 3058, 2924 cm^{-1} (C–H str), 2112 (C=N str), 1571 (arom C=C str) cm^{-1}. ES-MS: *m*/*z* = 745 [M – CNS]$^+$. $C_{39}H_{33}NP_2PtS$ (804.79): calcd. C 58.20, H 4.13, N 1.74, P 7.70; found C 58.01, H 4.28, N 1.79, P 7.94.

15: FAB-MS: *m*/*z* = 852 [M]$^+$.

***cis*-[Pt(OCOMe)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (9):** Silver acetate (11 mg, 0.065 mmol) was added to a solution of **2** (50 mg, 0.068 mmol) in $CHCl_3$ (0.5 mL). The mixture was stirred in the dark for 15 min, and the precipitated AgCl was removed by centrifugation. The supernatant was concentrated to a small volume under reduced pressure, and *n*-pentane was added to precipitate a white solid. This was re-dissolved in CH_2Cl_2, re-precipitated with *n*-pentane, washed with *n*-pentane and dried in vacuo to give complex **9** as a colourless solid (43 mg, 83%). ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, Me), 2.31 (s, 3 H, Me), 2.33 (s, 3 H, Me), 6.7–8.0 (m, 27 H, arom) ppm. IR (hexachlorobutadiene): $\tilde{\nu}$ = 3054, 2921 (C–H str), 1628 (C=O str), 1311 (C–O str) cm^{-1}. FAB-MS: *m*/*z* = 745 [M – OCOMe]$^+$.

***cis*-[Pt(OCOPh)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (10):** This was prepared similarly to **9**, with use of silver benzoate (15 mg, 0.065 mmol). The product was precipitated with *n*-hexane instead of *n*-pentane. The yield was 50 mg (91%). ^{1}H NMR (CDCl$_3$): δ = 2.31 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.6–8.0 (m, 32 H, arom) ppm. IR (hexachlorobutadiene): $\tilde{\nu}$ = 3056, 2915 (C–H str), 1712, 1633 (C=O str), 1336 (C–O str) cm^{-1}. ES-MS: *m*/*z* = 867 [M]$^+$. $C_{45}H_{38}O_2P_2Pt$ (867.82): calcd. C 62.28, H 4.41, P 7.14; found C 62.48, H 4.69, P 7.37. The *trans*-isomer was formed quantitatively in C_6D_6 after 24 h. ^{31}P NMR (C_6D_6): δ = 27.4 [d, *J*(P-P) = 455 Hz, *J*(Pt-P) = 3257 Hz], –53.0 [d, *J*(P-P) = 455 Hz, *J*(Pt-P) = 2514 Hz] ppm.

***cis*-[Pt(OH)(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (8):** Freshly prepared, moist silver oxide (ca. 150 mg, large excess) was added to a solution of **2** (50 mg, 0.063 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred in the dark for 3 d. Workup as for **9** gave a white solid (48 mg) consisting mainly of **8** contaminated with ca. 5% of **2**. Selected ^{1}H NMR (CD_2Cl_2) data: δ = 1.25 (br. s, 1 H, OH), 2.30 (s, 3 H, Me), 2.33 (s, 3 H, Me), 6.8–8.2 (m, 27 H, arom) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ = –4205 [dd, *J*(Pt-P) = 2008, 2803 Hz] ppm. IR (Nujol): $\tilde{\nu}$ = 3657 cm^{-1} (O–H str), 3048 (C–H str), 1570 (arom C=C str), 1027 (O–H def), 725 (C–H def) cm^{-1}. ES-MS: *m*/*z* = 763 [M – H]$^+$.

***cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] [X = F (7), CN (11)]:** These were prepared similarly to **8** from **2** (50 mg, 0.063 mmol) in dry CH_2Cl_2 and AgF (9 mg, 0.071 mmol) or AgCN (9 mg, 0.067 mmol), respectively, the mixtures being stirred for 3 d in the case of **7** and 3 h in the case of **11**. Workup as for complex **9** gave **7** (33 mg, 68%) and **11** (45 mg, 91%) as white solids.

7: ^{1}H NMR (CD_2Cl_2): δ = 2.32 (s, 3 H, Me), 2.33 (s, 3 H, Me), 6.6–7.7 (m, 27 H, arom) ppm. ^{19}F NMR (CD_2Cl_2): δ –285.1 [dd, *J*(P-F) = 26.1, 162.1 Hz, *J*(Pt-F) = 241 Hz] ppm. ^{195}Pt{^{1}H} NMR (CD_2Cl_2): δ = –4342 [ddd, *J*(Pt-P) = 1999, 3376 Hz, *J*(Pt-F) = 235 Hz] ppm. FAB-MS: *m*/*z* = 746 [M – F]$^+$. $C_{38}H_{33}FP_2Pt$ (765.71): calcd. C 59.61, H 4.34, P 8.09; found C 59.23, H 4.57, P 8.09.

11: ^{1}H NMR (CDCl$_3$): δ = 1.51 (br. s, 2 H, H$_2$O), 2.33 (s, 3 H, Me), 2.35 (s, 3 H, Me), 6.8–8.3 (m, 27 H, arom) ppm. IR (KBr): $\tilde{\nu}$ = 3438 cm^{-1} (O–H str), 3053, 2918 (C–H str), 2128 (C≡N str), 1571 (arom C=C str), 725 (C–H def) cm^{-1}. MALDI-MS: *m*/*z* = 772 [M]$^+$. $C_{39}H_{33}NP_2Pt \cdot H_2O$ (790.75): calcd. C 59.24, H 4.46, N 1.77, P 7.83; found C 59.19, H 4.45, N 1.77, P 7.92. X-ray quality crystals were grown from benzene/*n*-pentane.

***cis*-[Pt(κ*N*-NO$_2$)(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)] (16):** A solution of *cis*-[Pt(THF)(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)]BF$_4$ (**17**) was generated in situ by treatment of a solution of **2** (50 mg, 0.063 mmol) in CHCl$_3$ (0.5 mL) containing a drop of THF with AgBF$_4$ (12.4 mg, 0.063 mmol). The AgCl was removed by centrifugation, and the solution was treated with a solution of NaNO$_2$ (13 mg, 0.188 mmol) in methanol (4 mL). The solvents were removed in vacuo, and the residue was extracted with CH_2Cl_2. Repeated attempts to isolate a solid by concentration to a small volume and addition of *n*-hexane gave an orange oil. Finally, the oil was extracted with several portions of *n*-hexane, and the extracts were concentrated to dryness to give **16** as an off-white solid (47 mg, 92%). ^{1}H NMR (CDCl$_3$): δ = 2.26 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.8–8.0 (m, 27 H, arom) ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2949, 2918 (C–H str), 1570 (arom C=C str), 1384, 1331 (NO$_2$ str), 817 (NO$_2$ def), 725 (C–H def) cm^{-1}. FAB-MS: *m*/*z* = 746 [M – NO$_2$]$^+$. $C_{38}H_{33}NO_2P_2Pt$ (792.71): calcd. C 57.58, H 4.20, N 1.77, P 7.81; found C 57.89, H 4.48, N 1.78, P 7.83.

***cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)$_2$]BF$_4$ (34):** A stirred solution containing **2** (50 mg, 0.063 mmol) and PPh$_2$-4-tol (18 mg, 0.065 mmol) in CHCl$_3$ was treated with AgBF$_4$ (12.4 mg, 0.063 mmol). After 5 min, the precipitated AgCl was removed by centrifugation, and the supernatant liquid was concentrated. Addition of diethyl ether precipitated a white solid, which was purified by dissolution in CH_2Cl_2 and re-precipitated with diethyl ether. The solid was washed with diethyl ether and *n*-hexane, and dried in vacuo. The yield of **34** was 66 mg (93%). ^{1}H NMR (CDCl$_3$): δ = 1.56 (br. s, 2 H, H$_2$O), 1.75 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.37 (s, 3 H, Me), 6.4–7.8 (m, 41 H, arom) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ = –4377 [ddd, *J*(Pt-P) = 2007, 2135, 2846 Hz] ppm. MALDI-MS: *m*/*z* = 1021 [M – BF$_4$]$^+$. $C_{57}H_{50}BF_4P_3Pt \cdot H_2O$ (1127.85): calcd. C 60.70, H 4.65, P 8.24; found C 60.35, H 4.64, P 8.42. X-ray quality crystals were grown from CH_2Cl_2/benzene/*n*-pentane.

The following complexes *cis*-[PtL(κ^2-C_6H_3-5-Me-2-PPh$_2$)(PPh$_2$-4-tol)]BF$_4$ were prepared as white solids similarly to **34** on the same scale.

L = AsPh$_3$ (35): 71 mg (97%) from AsPh$_3$ (20 mg, 0.065 mmol). ^{1}H NMR (CDCl$_3$): δ = 1.55 (br. s, 4 H, H$_2$O), 1.76 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.4–7.7 (m, 42 H, arom) ppm. MALDI-MS: *m*/*z* = 1051 [M – BF$_4$]$^+$. $C_{56}H_{48}AsBF_4P_2Pt \cdot 2H_2O$ (1175.79): calcd. C 57.21, H 4.46, P 5.27; found C 57.25, H 4.35, P 5.66.

L = SbPh$_3$ (36): 73 mg (96%) from SbPh$_3$ (23 mg, 0.065 mmol). ^{1}H NMR (CDCl$_3$): δ = 1.51 (br. s, 2 H, H$_2$O), 1.72 (s, 3 H, Me), 2.21 (s, 3 H, Me), 6.5–7.6 (m, 42 H, arom) ppm. MALDI-MS: *m*/*z* = 1097 [M – BF$_4$]$^+$. $C_{56}H_{48}BF_4P_2PtSb \cdot H_2O$ (1204.59): calcd. C 55.84, H 4.18, P 5.14; found C 55.37, H 4.15, P 5.32.

L = Ph$_3$PO (18): 71 mg (97%) from Ph$_3$PO (20 mg, 0.065 mmol). ^{1}H NMR (CDCl$_3$): δ = 1.78 (s, 3 H, Me), 2.28 (s, 3 H, Me), 6.7–7.8 (m, 42 H, arom) ppm. FAB-MS: *m*/*z* = 1042 [M – BF$_4$]$^+$.

L = Ph$_3$PS (32): 53 mg (74%) from Ph$_3$PS (19 mg, 0.064 mmol). ^{1}H NMR (CDCl$_3$): δ = 1.50 (br. s, 2 H, H$_2$O), 1.75 (s, 3 H, Me), 2.25 (s, 3 H, Me), 6.7–7.8 (m, 42 H, arom) ppm. FAB-MS: *m*/*z* = 1042 [M – BF$_4$]$^+$. $C_{56}H_{48}BF_4P_3PtS \cdot H_2O$ (1145.88): calcd. C 58.70, H 4.40, P 8.11; found C 58.76, H 4.41, P 8.40.

L = Ph$_3$PSe (33): 71 mg (97%) from Ph$_3$PSe (20 mg, 0.065 mmol). ^{1}H NMR (CDCl$_3$): δ = 1.79 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.8–7.7 (m, 42 H, arom) ppm. ES-MS: *m*/*z* = 1087 [M – BF$_4$]$^+$. $C_{56}H_{48}BF_4P_3PtSe$ (1174.76): calcd. C 57.26, H 4.12, P 7.91; found C 57.07, H 4.18, P 7.89.

L = P(OPh)$_3$ (37): 61 mg (83%) of off-white solid obtained by use of one drop of P(OPh)$_3$. ^{1}H NMR (CDCl$_3$): δ = 2.31 (s, 3 H, Me), 2.34 (s, 3 H, Me), 6.6–8.0 (m, 42 H, arom) ppm. ES-MS: *m*/*z* = 1056 [M – BF$_4$]$^+$.

L = P(OMe)$_3$ (38): White solid (59 mg) from P(OMe)$_3$ (7.5 µL, 0.063 mmol). The ^{31}P NMR spectrum showed this to contain ca. 30% of the bis(phosphite) complex arising from displacement of the PPh$_2$-4-tol ligand, together with smaller amounts of unidentified impurities. Selected ^{1}H NMR (CDCl$_3$) data: δ = 2.36 (s, 3 H, tolyl Me), 2.37 (s, 3 H, tolyl Me), 3.56 [d, *J*(P-H) = 12.3 Hz, 9 H, 3 OMe], 6.8–7.6 (m, 27 H, arom) ppm. ES-MS: *m*/*z* = 870 [M – BF$_4$]$^+$.

L = SMe$_2$ (27): 55 mg (96%) by use of 1 drop of SMe$_2$. ^{1}H NMR (CDCl$_3$): δ = 1.56 (br. s, 1 H, H$_2$O), 2.31 (s, 3 H, tolyl Me), 2.32, 2.35 [2 s, 6 H, SMe$_2$ *J*(Pt-H) = 40.6 Hz], 2.34 (s, 3 H, tolyl Me), 6.8–8.0 (m, 42 H, arom) ppm. ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ = –3675 [dd, *J*(Pt-P) = 2007, 2840 Hz] ppm. FAB-MS: *m*/*z* = 808 [M – BF$_4$]$^+$. $C_{40}H_{39}BF_4P_2PtS \cdot 0.5H_2O$ (904.65): calcd. C 53.11, H 4.46, P 6.85; found C 53.29, H 4.43, P 7.23.

L = THT (30): Addition of 1 drop of THT gave a white solid from which adhering THT could not be removed, even by repeated washing with diethyl ether or drying in vacuo. ^{1}H NMR (CDCl$_3$): δ = 1.50 (br. m, 4 H, CH$_2$CH$_2$) 2.23 (s, 3 H, Me), 2.35 (s, 3 H, Me), 2.85 [br. m, 4 H, CH_2SCH_2, *J*(Pt-H) ≈ 40 Hz], 6.7–7.5 (m, 27 H, arom) ppm.

L = CO (39): Carbon monoxide was bubbled through a solution of **2** in $CHCl_3$ or $CDCl_3$ to which $AgBF_4$ (12.4 mg, 0.063 mmol) had been added. After 5 min, a precipitate of AgCl had formed. Attempts to isolate **39** from the supernatant liquid failed, so spectroscopic data were obtained in situ. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* –3631 [dd, *J*(Pt-P) = 1832, 2599 Hz] ppm.

L = MeCN (26): A solution of **2** in C_6D_6 or $CDCl_3$ containing a drop of acetonitrile was treated with $AgBF_4$ (12.4 mg, 0.063 mmol). The ^{31}P NMR spectrum was acquired after 30 min. The product decomposed on attempted isolation. After 24 h in solution, complete isomerisation to the *trans*-isomer had occurred. ^{31}P NMR (C_6D_6): *δ* = 23.7 [d, *J*(P-P) = 392 Hz, *J*(Pt-P) = 3005 Hz], –59.3 [*J*(P-P) = 392 Hz, *J*(Pt-P) = 2088 Hz] ppm.

The corresponding, similarly generated complexes containing L = SEt_2 (**28**), SPh_2 (**29**), DMSO (**31**), MeC≡CMe (**41**), PhC≡CPh (**42**) and THF (**17**) also could not be isolated. Their ^{31}P NMR spectra were obtained in situ.

L = NH_3 (19): $AgBF_4$ (12.4 mg, 0.063 mmol) was added to a solution of **2** (50 mg, 0.063 mmol) in $CHCl_3$ (0.5 mL) containing 1 drop of THF. The precipitated AgCl was removed by centrifugation, and the supernatant liquid, after being decanted, was treated with 1 drop of concentrated aqueous NH_3. The solution was concentrated to a small volume under reduced pressure. Addition of diethyl ether precipitated a white solid, which was purified by dissolution in CH_2Cl_2 and re-precipitation with diethyl ether. The solid was washed with *n*-pentane and dried in vacuo. The yield was 43 mg (80%). ^1H NMR ($CDCl_3$): *δ* = 2.32 (s, 6 H, 2 Me), 3.24 [br. s, 3 H, NH_3, *J*(Pt-H) ≈ 40 Hz], 6.8–7.8 (m, 27 H, arom) ppm. FAB-MS: *m*/*z* = 764 $[M - BF_4]^+$. $C_{38}H_{36}BF_4NP_2Pt$ (850.54): calcd. C 53.66, H 4.27, N 1.65, P 7.28; found C 53.45, H 4.31, N 1.47, P 7.46.

L = NEt_3 (20): The same procedure was used as for complex **19**, with 1 drop of NEt_3 in place of NH_3. Addition of diethyl ether gave a semi-solid that was purified by repeated washing with diethyl ether and *n*-pentane, and drying in vacuo. The yield was 51 mg (94%). ^1H NMR ($CDCl_3$): *δ* = 1.29 [t, *J*(H-H) = 7.3 Hz, 9 H, *Me*CH_2N], 2.06 (s, 3 H, tolyl Me), 2.28 (s, 3 H, tolyl Me), 3.03 (br. d, 6 H, MeCH_2N), 6.7–8.7 (m, 27 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –4171 [dd, *J*(Pt-P) = 1921, 3304 Hz] ppm. ES-MS: *m*/*z* = 745 $[M - NEt_3 - BF_4]^+$. $C_{44}H_{44}BF_4NP_2Pt$ (930.67): calcd. C 56.54, H 5.18, N 1.50, P 6.63; found C 52.98, H 4.88, N 1.41, P 6.95. Carbon analyses were consistently low, possibly owing to incomplete combustion.

The same procedure as for complex **19** was used for the following complexes.

L = $PhNH_2$ (21): Off-white solid (54 mg, 93%) from 1 drop of freshly distilled aniline. ^1H NMR ($CDCl_3$): *δ* = 2.31 (s, 3 H, Me), 2.32 (s, 3 H, Me), 6.14 [br. s, *J*(Pt-H) ≈ 40 Hz, 2 H, NH_2], 6.7–7.7 (m, 32 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3855 [dd, *J*(Pt-P) = 2018, 3067 Hz] ppm. ES-MS: *m*/*z* = 840 $[M - BF_4]^+$.

L = *o*-$MeC_6H_4NH_2$ (22): Pale red solid (52 mg, 88%) from 1 drop of freshly distilled *o*-toluidine. ^1H NMR ($CDCl_3$): *δ* = 2.13 (s, 3 H, *Me*$C_6H_4NH_2$), 2.22 (s, 3 H, tolyl Me), 2.30 (s, 3 H, tolyl Me), 5.93 [br. s, *J*(Pt-H) ≈ 40 Hz, 2 H, NH_2], 6.8–7.6 (m, 31 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3896 [dd, *J*(Pt-P) = 2017, 3100 Hz] ppm. ES-MS: *m*/*z* = 854 $[M - BF_4]^+$.

L = *m*-$MeC_6H_4NH_2$ (23): Purple solid (54 mg, 92%) from one drop of freshly distilled *m*-toluidine. ^1H NMR ($CDCl_3$): *δ* = 2.23 (s, 3 H, Me), 2.24 (s, 3 H, Me), 2.35 (s, 3 H, Me), 6.21 [br. s, *J*(Pt-H) ≈ 40 Hz, 2 H, NH_2], 6.5–7.8 (m, 31 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3884 [dd, *J*(Pt-P) = 2058, 3035 Hz] ppm. ES-MS: *m*/*z* = 854 $[M - BF_4]^+$.

L = *p*-$MeC_6H_4NH_2$ (24): Red solid (54 mg, 92%) from freshly sublimed *p*-toluidine (7 mg, 0.065 mmol). ^1H NMR ($CDCl_3$): *δ* = 2.24 (s, 3 H, Me), 2.32 (s, 6 H, 2 Me), 6.06 [br. s, *J*(Pt-H) ≈ 43 Hz, 2 H, NH_2], 6.6–7.6 (m, 31 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3882 [dd, *J*(Pt-P) = 2075, 3016 Hz] ppm. ES-MS: *m*/*z* = 854 $[M - BF_4]^+$.

L = C_5H_5N (25): Off-white solid (51 mg, 88%) from 1 drop of pyridine. ^1H NMR ($CDCl_3$): *δ* = 2.19 (s, 3 H, Me), 2.31 (s, 3 H, Me), 6.3–7.6 (m, 27 H, arom), 7.93 [dd, *J*(H-H) = 1.5, 7.7 Hz, 2 H, *m*-H of C_5H_5N], 8.39 [br. m, *J*(Pt-H) ≈ 25 Hz, 2 H, *o*-H of C_5H_5N], 8.75 [dd, *J*(H-H) = 1.5, 6.3 Hz, 1 H, *p*-H of C_5H_5N] ppm. FAB-MS: *m*/*z* = 825 $[M - BF_4]^+$.

L = *t*BuNC (40): Off-white solid (41 mg, 71%) from 1 drop of *tert*-butyl isocyanide. ^1H NMR ($CDCl_3$): *δ* = 1.34 (s, 9 H, *t*Bu), 2.39 (s, 3 H, tolyl Me), 2.40 (s, 3 H, tolyl Me), 6.8–7.7 (m, 27 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3552 [q of 1:1:1 t, *J*(Pt-P) = 1844, 2056 Hz, *J*(Pt-N) = 80.2 Hz] ppm. IR (hexachlorobutadiene): ṽ = 3047, 2981, 2915 (C–H str), 2212 (C≡N str), 1566 (arom C=C str), 725 (C–H def) cm^{-1}. ES-MS: *m*/*z* = 829 $[M - BF_4]^+$.

***cis*-[PtMe(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (43):** Under dry argon, a stirred solution of **2** (80 mg, 0.102 mmol) in THF (5 mL) was treated dropwise with methyllithium (1.6 M in diethyl ether, 70 μL, 0.120 mmol). The mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo, and the compound was extracted from the residue with CH_2Cl_2 (5 mL). Concentration to about half volume and addition of methanol gave **43** as a colourless solid (59 mg, 76%). ^1H NMR ($CDCl_3$): *δ* = 0.95 [t, *J*(P-H) = 7.1 Hz, *J*(Pt-H) = 74.7 Hz, 3 H, Pt-Me], 2.31 (s, 3 H, tolyl Me), 2.33 (s, 3 H, tolyl Me), 6.9–8.0 (m, 27 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –4156 [dd, *J*(Pt-P) = 1127, 2132 Hz] ppm. IR (KBr): ṽ = 3050, 3018, 2918, 2873 (C–H str), 1571 (arom C=C str), 1202 (Pt–Me def), 724 (C–H def) cm^{-1}. FAB-MS: *m*/*z* = 762 $[M]^+$. X-ray quality crystals were grown from benzene/*n*-pentane.

***cis*-[PtPh(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (44):** This was prepared similarly to **43** by reaction of **2** (80 mg, 0.102 mmol) in diethyl ether with phenyllithium (1.0 M in diethyl ether/benzene, 103 μL, 0.103 mmol) to give **44** as a white solid (61 mg, 72%). ^1H NMR ($CDCl_3$): *δ* = 2.35 (s, 3 H, Me), 2.36 (s, 3 H, Me), 6.8–8.3 (m, 32 H, arom) ppm. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): *δ* = –3741 [dd, *J*(Pt-P) = 1042, 2067 Hz] ppm. FAB-MS: *m*/*z* = 823 $[M]^+$.

***cis*-[Pt(C_6F_5)(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (45):** A solution of *n*-butyllithium (1.6 M in hexanes, 0.2 mL, 0.32 mmol) was added to a stirred solution of C_6F_5Br (79 mg, 0.32 mmol) in diethyl ether (5 mL) at –78 °C under dry argon. Stirring was continued at –78 °C for 1 h. To this solution of C_6F_5Li, the trifluoroacetato complex **6** was added, and the mixture was stirred at –78 °C for 30 min and at room temperature for 1 h. The turbid solution was treated with 1 drop of methanol, and the solvents were removed in vacuo. The residue was extracted with toluene, and the solution was chromatographed on a silica gel column. The fraction that eluted with toluene was concentrated to a small volume under reduced pressure, and *n*-pentane was added to precipitate a white solid. This was isolated by filtration, washed with *n*-pentane, and dried in vacuo to give **45** as a monohydrate (136 mg, 83%). ^1H NMR ($CDCl_3$): *δ* = 1.54 (br. s, 2 H, H_2O), 2.19 (s, 3 H, Me), 2.28 (s, 3 H, Me), 6.6–7.7 (m, 27 H, arom) ppm. ^{19}F NMR ($CDCl_3$): *δ* = –116.4 [m, *o*-F, *J*(Pt-F) = 406 Hz], –164.4 [t, *p*-F, *J*(Pt-F) = 16.3 Hz], –165.2 (m, *m*-F) ppm. IR (KBr): ṽ = 3435 cm^{-1} (O–H str), 3053, 3022, 2920

(C–H str), 1633 (O–H def), 1572 (arom C=C str), 1056, 953, 789 (C–F modes), 724 (C–H def) cm^{-1}. FAB-MS: m/z = 914 [M]$^+$. $C_{44}H_{33}F_5P_2Pt\cdot H_2O$ (931.78): calcd. C 57.27, H 3.71, P 6.71; found C 57.45, H 3.69, P 6.88. X-ray quality crystals were grown from benzene/*n*-pentane.

Supporting Information (see footnote on the first page of this article): Molecular structures of **11**, **43**, and **34**.

---

[1] A. Pidcock, R. E. Richards, L. M. Venanzi, *J. Chem. Soc. A* **1966**, 1707–1710.
[2] F. Basolo, R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., Wiley, New York, **1967**, chapter 5.
[3] O. F. Wendt, L. I. Elding, *J. Chem. Soc., Dalton Trans.* **1997**, 4725–4731.
[4] N. Kuznik, O. F. Wendt, *J. Chem. Soc., Dalton Trans.* **2002**, 3074–3078.
[5] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422, and references therein.
[6] F. H. Allen, A. Pidcock, *J. Chem. Soc. A* **1968**, 2700–2704.
[7] F. H. Allen, A. Pidcock, C. R. Waterhouse, *J. Chem. Soc. A* **1970**, 2087–2093.
[8] F. H. Allen, S. N. Sze, *J. Chem. Soc. A* **1971**, 2054–2056.
[9] T. G. Appleton, M. A. Bennett, *Inorg. Chem.* **1978**, *17*, 738–747.
[10] K. D. Tau, D. W. Meek, *Inorg. Chem.* **1979**, *18*, 3574–3580.
[11] G. G. Mather, A. Pidcock, G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.* **1973**, 2095–2099.
[12] L. J. Manojlović-Muir, K. W. Muir, *Inorg. Chim. Acta* **1974**, *10*, 47–49.
[13] P. B. Hitchcock, B. Jacobson, A. Pidcock, *J. Chem. Soc., Dalton Trans.* **1977**, 2043–2048.
[14] L. Manojlović-Muir, K. W. Muir, T. Solomun, *J. Organomet. Chem.* **1977**, *142*, 265–280.
[15] P. Sharma, A. Cabrera, M. Sharma, C. Alvarez, J. L. Arias, R. M. Gomez, S. Hernandez, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2330–2334.
[16] M. H. Johansson, A. Oskarsson, K. Lärqvist, F. Kiriakidou, P. Kapoor, *Acta Crystallogr., Sect. C* **2001**, *57*, 1053–1055.
[17] S. Otto, M. H. Johansson, *Inorg. Chim. Acta* **2002**, *329*, 135–140.
[18] K. R. Dixon, K. C. Moss, M. A. R. Smith, *J. Chem. Soc., Dalton Trans.* **1975**, 990–998, and references therein.
[19] M. A. Cairns, K. R. Dixon, G. A. Rivett, *J. Organomet. Chem.* **1979**, *171*, 373–385, and references therein.
[20] R. A. Michelin, R. Ros, *J. Chem. Soc., Dalton Trans.* **1989**, 1149–1159.
[21] M. A. Bennett, S. K. Bhargava, J. Messelhäuser, S. H. Privér, L. L. Welling, A. C. Willis, *Dalton Trans.* **2007**, 3158–3169.
[22] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.
[23] M. A. Bennett, D. L. Milner, *J. Am. Chem. Soc.* **1969**, *91*, 6983–6994.
[24] D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1977**, 797–804.
[25] D. M. Adams, J. Chatt, J. Gerratt, A. D. Westland, *J. Chem. Soc. A* **1964**, 734–739.
[26] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, **1979**, p. 96.
[27] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, part B, p. 88.
[28] C. Tessier, F. D. Rochon, *Inorg. Chim. Acta* **2001**, *322*, 37–46.
[29] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, part B, pp. 59–62.
[30] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.
[31] B. E. Mann, B. L. Shaw, N. I. Tucker, *J. Chem. Soc. A* **1971**, 2667–2673.
[32] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, **1979**, p. 97.
[33] R. Romeo, *Comments Inorg. Chem.* **2002**, *23*, 79–100.
[34] K. R. Dixon, J. J. McFarland, *J. Chem. Soc., Chem. Commun.* **1972**, 1274–1275.
[35] M. A. Cairns, K. R. Dixon, J. J. McFarland, *J. Chem. Soc., Dalton Trans.* **1975**, 1159–1164.
[36] R. J. Cross, M. Haupt, D. S. Rycroft, J. M. Winfield, *J. Organomet. Chem.* **1999**, *587*, 195–199.
[37] N. M. Doherty, N. W. Hoffman, *Chem. Rev.* **1991**, *91*, 553–573.
[38] E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425–3468.
[39] A. Mezzetti, C. Becker, *Helv. Chim. Acta* **2002**, *85*, 2686–2703.
[40] J. Howard, P. Woodward, *J. Chem. Soc., Dalton Trans.* **1973**, 1840–1843.
[41] D. R. Russell, M. A. Mazid, P. A. Tucker, *J. Chem. Soc., Dalton Trans.* **1980**, 1737–1742.
[42] H. Donath, E. V. Avtomonov, I. Sarraje, K. H. von Dahlen, M. El-Essawi, J. Lorberth, B. S. Seo, *J. Organomet. Chem.* **1998**, *559*, 191–196.
[43] P. Nilsson, F. Plamper, O. F. Wendt, *Organometallics* **2003**, *22*, 5235–5242.
[44] D. P. Arnold, M. A. Bennett, *J. Organomet. Chem.* **1980**, *199*, 119–135.
[45] H. E. Bryndza, W. Tam, *Chem. Rev.* **1988**, *88*, 1163–1188, and references therein.
[46] M. A. Cairns, K. R. Dixon, M. A. R. Smith, *J. Organomet. Chem.* **1977**, *135*, C33–C34.
[47] R. Faggiani, B. Lippert, C. J. L. Lock, B. Rosenberg, *Inorg. Chem.* **1978**, *17*, 1941–1945.
[48] D. M. Barlex, R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.* **1972**, 1436–1439.
[49] B. Milani, E. Alissio, G. Mestroni, A. Sommazzi, F. Garbassi, E. Zangrando, N. Bresciani-Pahor, L. Randaccio, *J. Chem. Soc., Dalton Trans.* **1994**, 1903–1911.
[50] D. A. Redfield, L. W. Cary, J. H. Nelson, *Inorg. Chem.* **1975**, *14*, 50–59.
[51] C. T. Hunt, A. L. Balch, *Inorg. Chem.* **1982**, *21*, 1242–1246.
[52] E. Grimley, D. W. Meek, *Inorg. Chem.* **1986**, *25*, 2049–2053.
[53] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, part B, p. 122.
[54] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, part B, pp. 116–121.
[55] P. F. Kelly, I. P. Parkin, R. N. Sheppard, J. D. Woollins, *Heteroat. Chem.* **1991**, *2*, 301–305.
[56] S. Ford, M. R. Lewtas, C. P. Morley, M. Di Vaira, *Eur. J. Inorg. Chem.* **2000**, 933–938.
[57] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, part B, pp. 48–53.
[58] W. Oberhauser, C. Bachmann, P. Brüggeller, *Inorg. Chim. Acta* **1995**, *238*, 35–43.
[59] T. V. O'Halloran, M. M. Roberts, S. J. Lippard, *Inorg. Chem.* **1986**, *25*, 957–964.
[60] H. C. S. Clark, J. Fawcett, J. H. Holloway, E. G. Hope, L. A. Peck, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **1998**, 1249–1252.
[61] R. Romeo, G. Alibrandi, *Inorg. Chem.* **1997**, *36*, 4822–4830, and references therein.
[62] D. C. Smith Jr, C. M. Haar, E. D. Stevens, S. P. Nolan, W. J. Marshall, K. Moloy, *Organometallics* **2000**, *19*, 1427–1433.
[63] M. Crespo, J. Sales, *J. Organomet. Chem.* **1987**, *322*, 405–411.
[64] R. Usón, M. A. Usón, S. Herrero, L. Rello, *Inorg. Chem.* **1998**, *37*, 4473–4476.
[65] F. Mohr, S. H. Privér, S. K. Bhargava, M. A. Bennett, *Coord. Chem. Rev.* **2006**, *250*, 1851–1888, and references therein.
[66] Y. Wang, *Acta Chim. Sin.* **1985**, *43*, 683–687.

[67] D. H. Farrar, G. Ferguson, *J. Crystallogr. Spectrosc. Res.* **1982**, *12*, 465–471.

[68] P. Kapoor, K. Lövqvist, A. Oskarsson, *J. Mol. Struct.* **1998**, *470*, 39–47.

[69] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, A. Rieder, P. Brüggeller, *Polyhedron* **1998**, *17*, 3211–3220.

[70] R. P. Hughes, J. T. Sweetser, M. D. Tawa, A. Williamson, C. D. Incarvito, B. Rhatigan, A. L. Rheingold, G. Rossi, *Organometallics* **2001**, *20*, 3800–3810.

[71] G. B. Deacon, P. W. Elliott, A. P. Erven, G. Meyer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 843–850.

[72] L. R. Falvello, J. Forniés, R. Navarro, A. Rueda, E. P. Urriolabeitia, *Organometallics* **1996**, *15*, 309–316.

[73] M. A. Bennett, T. Dirnberger, D. C. R. Hockless, E. Wenger, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **1998**, 271–278.

[74] S. Park, A. L. Rheingold, D. M. Roundhill, *Organometallics* **1991**, *10*, 615–623.

[75] G. Alibrandi, L. Scolaro, D. Minniti, R. Romeo, *Inorg. Chem.* **1990**, *29*, 3467–3472.

[76] R. J. Cross, M. F. Davidson, M. Rocamora, *J. Chem. Soc., Dalton Trans.* **1988**, 1147–1152.

[77] G. K. Anderson, H. C. Clark, J. A. Davies, *Inorg. Chem.* **1981**, *20*, 944–945.

[78] S. S. Zumdahl, R. S. Drago, *J. Am. Chem. Soc.* **1968**, *90*, 6669–6675.

[79] D. R. Armstrong, R. Fortune, P. G. Perkins, R. J. Dickinson, R. V. Parish, *Inorg. Chim. Acta* **1976**, *17*, 73–79.

[80] E. Shustorovich, *Inorg. Chem.* **1979**, *18*, 1030–1039.

[81] T. G. Appleton, J. R. Hall, S. F. Ralph, *Inorg. Chem.* **1985**, *24*, 4685–4693.

[82] R. Münzenberg, P. Rademacher, R. Boese, *J. Mol. Struct.* **1998**, *444*, 77–90.

[83] L. A. Latif, *J. Chem. Res. (S)* **1995**, 264.

[84] D. Moigno, W. Kiefer, B. Callejas-Gasper, J. Gil-Rubio, H. Werner, *New J. Chem.* **2001**, *25*, 1389–1397.

[85] M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, J. E. H. Ward, *J. Am. Chem. Soc.* **1973**, *95*, 8574–8583.

[86] M. H. Chisholm, H. C. Clark, *Inorg. Chem.* **1971**, *10*, 2557–2563.

[87] *COLLECT Software*, Nonius BV, Delft, The Netherlands, **1997–2001**.

[88] Z. Otwinowski, W. Minor, in *Methods in Enzymology* (Eds.: C. W. Carter Jr, R. M. Sweet), Acedemic Press, New York, **1997**, vol. 276, pp. 307–326.

[89] P. J. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. Smits, C. Smykalla, *The DIRDIF Program System*, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, **1992**.

[90] P. J. Beurskens, G. Beurskens, W. P. Bosman, R. S. de Gelder, S. García-Granda, R. O. Gould, J. M. Smits, *The DIRDIF 96 Program System*, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, **1996**.

[91] *TEXSAN, Single Crystal Structure Analysis Software*, version 1.8, Molecular Structure Corporation, The Woodlands, TX, **1992–1997**.

[92] D. J. Watkins, C. K. Prout, J. R. Carruthers, P. W. Betteridge, R. J. Cooper, *CRYSTALS Issue 11*, Chemical Crystallography Laboratory, Oxford, **2001**.

[93] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

Received: April 2, 2008