Sterically Hindered Metal Alkenyls. Part 1. Synthesis, Reactions, and Crystal and Molecular Structures of some Palladium and Platinum σ-Alkenyls *

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The compounds *trans*-$[PtBr\{C(C_{10}H_{15})=CH_2\}(PEt_3)_2]$ (**1**) ($C_{10}H_{15}$ = adamant-1-yl), *trans*-$[MBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$ [M = Pd (**2**) or Pt (**3**); $C_{10}H_7$ = naphth-1-yl], and *trans*-$[MBr\{C(Ph)=CMe_2\}(PEt_3)_2]$ [M = Pd (**4**) or Pt (**5**)] have been prepared from Grignard [for (**2**) and (**3**)] or lithium reagents [for (**1**), (**4**), and (**5**)] and appropriate dichlorobis(phosphine)metal derivatives. Full single-crystal *X*-ray data are reported for (**1**) and (**3**), and reveal unusually long Pt–C(sp^2) bonds. Insertion reactions into these M–C bonds occur with MeNC [for (**1**), (**3**), and (**5**)], and with CO [for (**1**) and (**3**)]; the latter, the first reported insertion into a Pt–C(sp^2) bond, occurs under mild conditions as expected for the abnormally long M–C bonds.

Grignard and lithium reagents have been reported for trans-alkenylations to Ni^{II}, Pd^{II}, or Pt^{II} only with polyhalogenated alkenyls.[1] Most other documented syntheses employed the oxidative-addition reaction.[2] No results on 2,2-disubstituted σ-alkenyls have been published, and none related to compounds with very bulky α-substituents. We report here on some Pd^{II} and Pt^{II} non-halogenated σ-alkenyls obtained by the Grignard or lithium route, which incorporate large α-substituents. For platinum, they display reactivity at the metal–carbon bond greater than that previously observed for either Pt–C(sp^2) or Pt–C(sp^3) species. This reactivity we ascribe in part to the bulky α-substituents incorporated, which, as the crystal data reveal, result in Pt–C bonds longer than hitherto observed.

Results and Discussion

The new chloroalkenes were obtained in good yield from the appropriate ketones by reaction with phosphorus pentachloride. Details for these and related compounds will be reported elsewhere. While $CCl(C_{10}H_{15})=CH_2$ [$C_{10}H_{15}$ = adamant-1-yl (tricyclo[3.3.1.1^{3,7}]dec-1-yl)] gave the Grignard reagent in tetrahydrofuran in excellent yield, the lithium reagent could not be so obtained satisfactorily. However, the bromoalkene afforded the lithio species in good yield in diethyl ether. Similarly, $CCl(C_{10}H_7)=CMe_2$ ($C_{10}H_7$ = naphth-1-yl) readily gave the Grignard reagent, but was converted to the iodide for preparation of the lithium compound.

Synthesis of Metal(II) *Alkenyls*.—Reaction of the lithioalkenes, prepared *in situ* from the bromides, with *cis*-$[PtCl_2(PEt_3)_2]$ afforded not the chloro- but the bromo-alkenyl metal complex [equation (1), R = $C(C_{10}H_{15})=CH_2$ (**1**) or $C(Ph)=CMe_2$ (**5**)].

$$cis\text{-}[PtCl_2(PEt_3)_2] + LiR \xrightarrow[(LiBr)]{Et_2O} trans\text{-}[PtBr(R)(PEt_3)_2] + LiCl \quad (1)$$

It is common for organylations of *cis*-platinum(II) dihalides to be accompanied by isomerisation to the *trans* isomers, and we presume that this happens initially, followed by the halogen exchange facilitated by the *trans* influence of the hydrocarbyl, and in keeping with the ligand preferences of the soft platinum(II) centre. However, the reaction course may not be simple, as indicated by the following observations: (*i*) the isolated yield of *ca.* 30% could not be increased either by raising the temperature or extending the reaction time to five days; (*ii*) the lithium reagent, under the same conditions does not react with the *trans* isomer of the platinum starting material; and (*iii*) the non-alkenylated metal is recovered mainly as the *trans*-dibromobis(phosphine) complex. Thus (*ii*) and (*iii*) together imply that halogen exchange must be at least comparable in rate with organylation, and explain the first point. It is noteworthy that the Cl/Br exchange occurs with geometrical isomerisation, unusual for platinum(II) substitutions,[3] and that the *trans* isomer is completely unreactive with LiR, presumably because of the bulk of R, since, for example, MgMeI reacts readily (90% yield).[4]

A similar Cl/Br exchange occurred in the Grignard synthesis shown in equation (2). In this case, the bromide originated from

$$cis\text{-}[PtCl_2(PEt_3)_2] + MgCl[C(C_{10}H_7)=CMe_2] \xrightarrow{Et_2O\ (MgBr_2)} trans\text{-}[PtBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2] + \text{'MgBrCl'} \quad (2)$$

1,2-dibromoethane used to initiate the (*in situ*) preparation of the magnesium reagent. It is interesting that the yield (88%) in this reaction appears to be uniquely high for an alkenylation at platinum.

The palladium compounds *trans*-$[PdBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$ (**2**) and *trans*-$[PdBr\{C(Ph)=CMe_2\}(PEt_3)_2]$ (**4**) were similarly prepared from *trans*-$[PdCl_2(PEt_3)_2]$ using magnesium or lithium reagents respectively, and in both cases the remaining chloride ligand was replaced by bromide, as above. In contrast to the platinum preparations, these proceed substantially to completion at −78 °C. The palladium starting material was reduced to metal with the lithium reagent $LiC(C_{10}H_{15})=CH_2$, the other products being free phosphine and the bromo-olefin.

Properties and Reactions.—The platinum alkenyls and (**4**) are colourless or pale yellow crystalline solids, stable to air, and thermally, up to their melting points. Compound (**2**) was isolated as an orange powder, which decomposed on standing at room temperature. This decomposition is believed to occur by reductive elimination of the bromo-olefin, which was identified in the decomposition products. Presumably the adamantyl-

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* *Supplementary data available* (No. SUP 56601, 4 pp.): thermal parameters, packing diagrams. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected data on the new Pt^{II} and Pd^{II} compounds

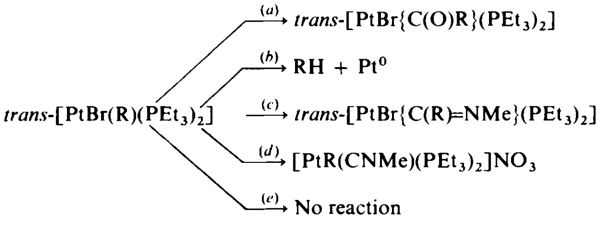
			Analysis[b] (%)				
Compound[a]	Yield (%)	M.p./ °C	C	H	Br	N	Form
(**1**) $[PtBr\{C(C_{10}H_{15})=CH_2\}(PEt_3)_2]$	30	190	42.5 (42.8)	7.0 (6.9)	11.9 (11.9)		Colourless crystalline
(**3**) $[PtBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$	88	181	45.6 (45.4)	6.3 (6.3)	10.3 (9.3)		Colourless crystalline
(**5**) $[PtBr\{C(Ph)=CMe_2\}(PEt_3)_2]$	25	137	40.8 (41.9)	6.5 (6.3)	10.8 (12.4)		Colourless crystalline
$[PtBr\{C[C(C_{10}H_{15})=CH_2]=NMe\}(PEt_3)_2]$	60	143					White crystalline
$[PtBr\{C[C(C_{10}H_7)=CMe_2]=NMe\}(PEt_3)_2]$	65	116	45.05 (45.8)	6.20 (6.3)		1.65 (1.9)	White crystalline
$[PtBr\{C[C(Ph)=CMe_2]=NMe\}(PEt_3)_2]$	85	117	41.6 (42.3)	6.30 (6.5)		2.05 (2.05)	Pale blue crystalline
$[PtBr\{C(O)(CPh=CMe_2)\}(PEt_3)_2]$	90	122	41.05 (41.2)	6.40 (6.40)	12.15 (11.9)		Yellow crystalline
(**4**) $[PdBr\{C(Ph)=CMe_2\}(PEt_3)_2]$	25	118	46.0 (47.6)	7.6 (7.6)	14.3 (14.4)		Pale yellow crystalline
(**2**) $[PdBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$	52	157					Orange powder at −20 °C, decomposes at room temperature

[a] $C_{10}H_{15}$ = adamant-1-yl, $C_{10}H_7$ = naphth-1-yl. [b] Calculated values in parentheses.

Table 2. Selected ^1H n.m.r. and i.r. data for the new alkenyl compounds

Compound		δ/p.p.m.	$\lvert ^nJ(Pt-H)\rvert$/Hz		ν(C=C)/ cm^{-1}	ν(C=X)/ cm^{-1}
(**1**) $[PtBr\{C(C_{10}H_{15})=CH_2\}(PEt_3)_2]$	$=C<H_{cis}$	4.83	$\lvert ^3J(Pt-H_{cis})\rvert$	88	1 565	
	H_{trans}	5.79	$\lvert ^3J(Pt-H)_{trans}\rvert$	161		
(**3**) $[PtBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$	$=C<Me_{cis}$	1.39, 1.41	$\lvert ^4J(Pt-H_{cis})\rvert$	*a*	1 590	
	Me_{trans}	2.21	$\lvert ^4J(Pt-H)_{trans}\rvert$	15		
(**5**) $[PtBr\{C(Ph)=CMe_2\}(PEt_3)_2]$	$=C<Me_{cis}$	2.06	$\lvert ^4J(Pt-H_{cis})\rvert$	7	1 590	
	Me_{trans}	2.38	$\lvert ^4J(Pt-H_{trans})\rvert$	7		
$[PtBr\{C[C(C_{10}H_{15})=CH_2]=NMe\}(PEt_3)_2]$	NMe	3.55	$\lvert ^4J(Pt-H)\rvert$	14.3		
	$=C<H_{cis}$	5.55	$\lvert ^3J(Pt-H_{cis})\rvert$	0	*a*	1 580[b]
	H_{trans}	6.98	$\lvert ^3J(Pt-H_{trans})\rvert$	0		
$[PtBr\{C[C(C_{10}H_7)=CMe_2]=NMe\}(PEt_3)_2]$	NMe	3.58	$\lvert ^4J(Pt-H)\rvert$	16.5		
	$=C<H_{cis}$	1.31	$\lvert ^4J(Pt-H_{cis})\rvert$	*a*	1 610	1 580[b]
	H_{trans}	2.22	$\lvert ^4J(Pt-H_{trans})\rvert$	8.25		
$[PtBr\{C[C(Ph)=CMe_2]=NMe\}(PEt_3)_2]$	NMe	3.55	$\lvert ^4J(Pt-H)\rvert$	14.3		
	$=C<Me_{cis}$	1.3	$\lvert ^4J(Pt-H)_{cis}\rvert$	6.13	1 615	1 580[b]
	Me_{trans}	2.12	$\lvert ^4J(Pt-H_{trans})\rvert$	8.17		
$[PtBr\{C(O)(CPh=CMe_2)\}(PEt_3)_2]$	$=C<Me_{cis}$	1.43	$\lvert ^4J(Pt-H_{cis})\rvert$	0	1 590	1 610[c]
	Me_{trans}	2.45	$\lvert ^4J(Pt-H_{trans})\rvert$	0		
(**4**) $[PdBr\{C(Ph)=CMe_2\}(PEt_3)_2]$	$=C<Me_{cis}$	1.94			1 590	
	Me_{trans}	2.18				
(**2**) $[PdBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$	$=C<Me_{cis}$	*a*			1 590	
	Me_{trans}	2.28				

[a] Could not be measured. [b] X = NMe. [c] X = O.



Scheme. (*a*) CO, R = $C(C_{10}H_{15})=CH_2$ or $C(Ph)=CMe_2$; (*b*) $LiAlH_4$, R = $C(C_{10}H_{15})=CH_2$; (*c*) MeNC, R = $C(C_{10}H_{15})=CH_2$, $C(C_{10}H_7)=CMe_2$, or $C(Ph)=CMe_2$; (*d*) $AgNO_3$, then MeNC, R = $C(C_{10}H_{15})=CH_2$; (*e*) with H_2, LiMe, C_2H_4, or $MeO_2CC\equiv CCO_2Me$, R = $C(C_{10}H_{15})=CH_2$

substituted compound behaves similarly, but elimination occurs at a lower temperature (bromo-olefin again produced). Thus it appears that the α-bulk is a major factor in determining the stability of the palladium alkenyls: the thermal stability order for α-substituents is Ph > $C_{10}H_7$ > $C_{10}H_{15}$, in harmony with the observed Pt–C bond lengths (see below).* The stability of the [(adamant-1-yl)ethenyl]platinum compounds we attribute to the greater M–C bond strength for this metal. For nickel, no alkenyls could be isolated. Analytical and other data are given in Table 1 for the new alkenyls and their derivatives. Both metathetical and insertion reactions were studied for compounds (**1**), (**3**), and (**5**), and the results are summarised in the Scheme. Products have been characterised analytically (Table 1) and spectroscopically (Table 2).

The CO insertions, which are the first reported for Pt–C(alkenyl) bonds, occur rapidly at room temperature and pressure, although with the adamantyl-substituted ligand the

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* See also, thermally stable *trans*-$[PdBr(CH=CHPh)(PPh_3)_2]$, M. K. Loan and J. K. Stille, *J. Am. Chem. Soc.*, 1981, **103**, 4175.

reaction did not go to completion. For compound (**5**), however, the insertion proceeds rapidly in the range 0—10 °C in diethyl ether, although no attempt has been made to enhance this reactivity by variation of solvent or conditions. Insertions into Pt–C(sp^3) bonds normally require much harsher conditions,[5] and it is tempting to account for the reactivity in terms of the observed Pt–C bond lengthening resulting from the bulky substituents. The reactivity order (**5**) > (**1**) ≫ (**3**) [(**3**) failing to react after prolonged times at ambient temperature] may be associated with lower steric crowding in a possible five-co-ordinate intermediate. However, such insertions are not mechanistically simple,[6,7] and no intermediate having a terminal CO ligand was observed. All three compounds give *N*-methylimino derivatives with MeNC, again under unusually mild conditions (room temperature, diethyl ether).[8–10]

With regard to the mechanism in this case, the addition of MeNC to (**1**) or (**3**) causes the release of free phosphine, and the precipitation (in low yield) of products showing i.r. bands for co-ordinated MeNC and alkenyl, but not of inserted isonitrile, and are therefore formulated as the phosphine replacement products [PtBr(CNMe)R(PEt$_3$)]. Analogous compounds, *viz*. [PtX(CO)R′(PMePh$_2$)], have been well characterised in some carbonylations,[7b] and three isomers identified. It has been shown,[7c] *e.g*. for [PtCl(CO)Ph(PMePh$_2$)], that only one of these isomers leads readily to the aroyl insertion product. The species isolated here did not react further during 24 h, but it may be that another isomer of [PtBr(CNMe)R(PEt$_3$)] is an intermediate in the insertion. The potential 1,2-insertion reagents ethene and dimethylacetylene dicarboxylate failed to react with (**1**) at ambient temperature, presumably requiring η^2-co-ordination prior to insertion, which is sterically hindered in these cases.

A silver nitrate suspension in diethyl ether did not effect complete bromide metathesis in (**1**) over 4 h. Subsequent treatment with MeNC therefore produced the insertion product, together with a material tentatively formulated as [Pt{C(C$_{10}$H$_{15}$)=CH$_2$}(CNMe)(PEt$_3$)$_2$]NO$_3$ on the basis of i.r. data: ν(C=N) 2 220, ν(C=C) 1 570, and ν(NO$_3$) (free ion) 1 390 cm^{-1}. No attempt was made to separate the products. An attempt to convert the bromide (**1**) into the corresponding hydride with LiAlH$_4$ (1.4 H per Pt in diethyl ether) at room temperature yielded, after an initial orange intermediate, free phosphine, platinum metal, and HC(C$_{10}$H$_{15}$)=CH$_2$. Presumably the hydrido(alkenyl)platinum species, like other hydrido(hydrocarbyls) of this metal, is unstable at ambient temperature.[11,*] Finally, in an effort to obtain a mixed alkenyl(alkyl)platinum(II) complex, (**1**) and (**5**) were treated with LiMe in diethyl ether. Even after 14 h reflux, no reaction was observed. Furthermore, treatment of *trans*-[PtI(Me)(PEt$_3$)$_2$] with LiC(C$_{10}$H$_{15}$)=CH$_2$ produced a small amount of *trans*-[PtI{C(C$_{10}$H$_{15}$)=CH$_2$}(PEt$_3$)$_2$] suggesting competition between alkyl and alkenyl on the metal, possibly occurring *via* oxidative addition to give platinum(IV).

Molecular Structures.—*X*-Ray analyses were carried out on compounds (**1**) and (**3**) to examine the effect of the bulky α-substituents on molecular geometry and the Pt–C(sp^2) bonds in particular. The structures are shown in Figures 1 and 2, and selected bond lengths and angles are presented in Tables 3 and 4.

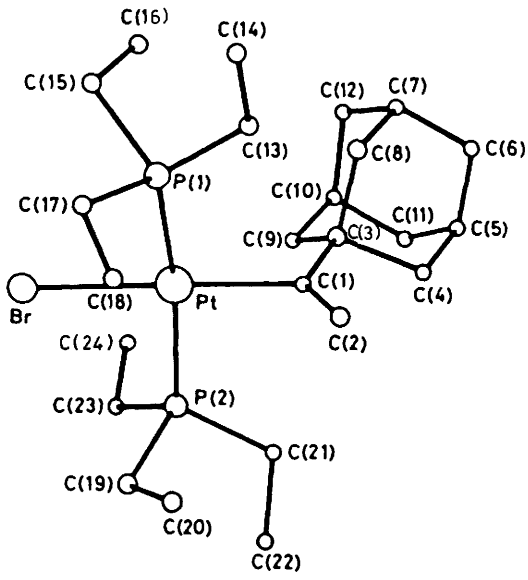

Figure 1. A single molecule of (**1**), showing the numbering scheme

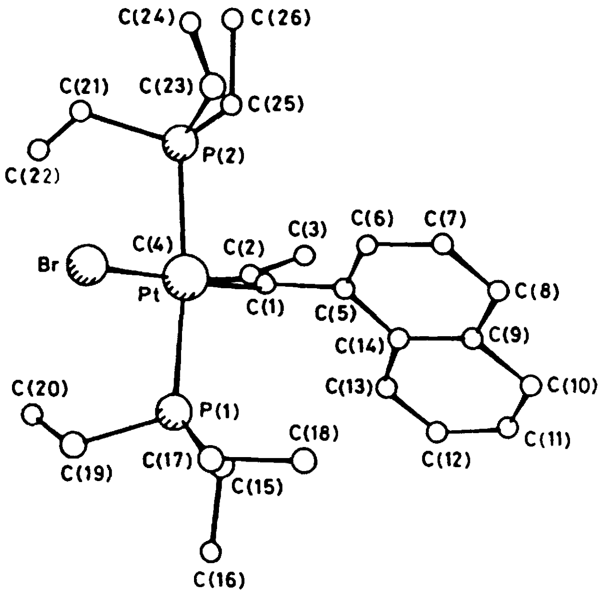

Figure 2. A single molecule of (**3**), showing the numbering scheme

Both structures show basic square-planar co-ordination about the metal atom, with considerable distortions due to the adamantyl or naphthyl substituents, which are larger for (**1**) than for (**3**). The effect of the α-bulk can be seen in (*i*) the long Pt–C(sp^2) bond lengths, (*ii*) the non-planarity of the platinum with its ligating atoms, (*iii*) the bond angles subtended at the metal, and (*iv*) the Pt–Br distance.

With regard to (*i*), the bond length for (**1**), of 2.14(2) Å is the longest yet found for a Pt–C bond, and is remarkable when allowance is made for the lesser radius of a trigonal carbon compared with that of a tetrahedral. The corresponding bond length in (**3**), of 2.086(18) Å, though smaller, is still substantially greater than in either [PtCl(CH=CH$_2$)(PEt$_2$Ph)$_2$] [2.032(23) Å][12] or [PtBr(CH=CHPh)(PPh$_3$)$_2$] [2.022(8) Å].[13] One of the phosphorus atoms is significantly bent back from the alkenyl ligand [point (*ii*)]. The adamantyl substituent in (**1**) is twisted with respect to the mean platinum co-ordination plane, so that the two CPtP angles are

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[*] We are grateful to a referee for drawing our attention to the fact that *trans*-hydrido(hydrocarbyl) complexes of platinum(II) can be isolated (D. P. Arnold and M. A. Bennett, *Inorg. Chem*., 1984, **23**, 2110), which is the expected stereochemistry here. Nevertheless, in the present case, no such species were isolable.

Table 3. Bond lengths (Å) and angles (°) for *trans*-$[PtBr\{C(C_{10}H_{15})=CH_2\}(PEt_3)_2]$ (**1**)

Pt–Br	2.549(2)[a]	C(9)–C(10)	1.60(4)
Pt–P(1)	2.301(5)	C(10)–C(11)	1.49(4)
Pt–P(2)	2.310(5)	C(10)–C(12)	1.53(4)
Pt–C(1)	2.14(2)	C(13)–P(1)	1.79(2)
C(1)–C(2)	1.29(3)	C(13)–C(14)	1.53(3)
C(1)–C(3)	1.54(3)	C(15)–P(1)	1.93(4)
C(3)–C(4)	1.60(3)	C(15)–C(16)	1.33(6)
C(3)–C(8)	1.54(3)	C(17)–P(1)	1.82(3)
C(3)–C(9)	1.43(3)	C(17)–C(18)	1.44(4)
C(4)–C(5)	1.54(4)	C(19)–P(2)	1.83(3)
C(5)–C(6)	1.46(4)	C(19)–C(20)	1.56(4)
C(5)–C(11)	1.53(4)	C(21)–P(2)	1.90(3)
C(6)–C(7)	1.46(4)	C(21)–C(22)	1.54(3)
C(7)–C(8)	1.60(3)	C(23)–P(2)	1.88(3)
C(7)–C(12)	1.39(4)	C(23)–C(24)	1.45(4)

Br–Pt–P(1)	87.6(1)	C(3)–C(9)–C(10)	113(2)
Br–Pt–P(2)	86.9(2)	C(9)–C(10)–C(11)	106(3)
Br–Pt–C(1)	176.9(6)	C(9)–C(10)–C(12)	105(3)
C(1)–Pt–P(1)	95.1(6)	C(11)–C(10)–C(12)	114(3)
C(1)–Pt–P(2)	90.8(6)	C(5)–C(11)–C(10)	109(3)
P(1)–Pt–P(2)	166.0(2)	C(7)–C(12)–C(10)	110(3)
Pt–C(1)–C(2)	117(2)	Pt–P(1)–C(13)	120.5(8)
Pt–C(1)–C(3)	114(2)	Pt–P(1)–C(15)	115.6(11)
C(2)–C(1)–C(3)	129(2)	Pt–P(1)–C(17)	109.7(9)
C(1)–C(3)–C(4)	106(2)	C(13)–P(1)–C(15)	103.8(14)
C(1)–C(3)–C(8)	112(2)	C(13)–P(1)–C(17)	107.3(12)
C(1)–C(3)–C(9)	117(2)	C(15)–P(1)–C(17)	97.1(14)
C(4)–C(3)–C(8)	100(2)	P(1)–C(13)–C(14)	120(2)
C(4)–C(3)–C(9)	110(2)	P(1)–C(15)–C(16)	112(4)
C(8)–C(3)–C(9)	109(2)	P(1)–C(17)–C(18)	115(2)
C(3)–C(4)–C(5)	109(2)	Pt–P(2)–C(19)	108.5(9)
C(4)–C(5)–C(6)	111(3)	Pt–P(2)–C(21)	119.5(8)
C(4)–C(5)–C(11)	107(3)	Pt–P(2)–C(23)	115.6(10)
C(6)–C(5)–C(11)	115(3)	C(19)–P(2)–C(21)	102.7(12)
C(5)–C(6)–C(7)	110(3)	C(19)–P(2)–C(23)	101.0(12)
C(6)–C(7)–C(8)	106(2)	C(21)–P(2)–C(23)	107.2(13)
C(6)–C(7)–C(12)	118(2)	P(2)–C(19)–C(20)	112(2)
C(8)–C(7)–C(12)	106(2)	P(2)–C(21)–C(22)	114(2)
C(3)–C(8)–C(7)	111(2)	P(2)–C(23)–C(24)	117(2)

$\langle C-C\rangle_{ethyl}$	1.48(8)[b]	$\langle C-P-C\rangle$	103(4)
$\langle C-C\rangle_{C_{10}H_{15}}$	1.51(7)	$\langle P-C-C\rangle$	115(3)
$\langle P-C\rangle$	1.8(5)	$\langle C-C-C\rangle_{C_{10}H_{15}}$	110(4)
		$\langle Pt-P-C\rangle$	115(5)

[a] Estimated standard deviations are in the last two significant figures (if $\leqslant 20$). [b] Estimated standard deviations of the mean are calculated from $\sigma^2 = [\Sigma(x_i - \bar{x})^2/(N - 1)]$ where x_i is the ith parameter and $\bar{x}$ is the mean of N equivalent parameters.

Table 4. Bond lengths (Å) and angles (°) for *trans*-$[PtBr\{C(C_{10}H_7)=CMe_2\}(PEt_3)_2]$ (**3**)

Pt–Br	2.537(2)	C(11)–C(12)	1.378(38)
Pt–P(1)	2.297(5)	C(12)–C(13)	1.390(28)
Pt–P(2)	2.320(5)	C(13)–C(14)	1.402(29)
Pt–C(1)	2.086(18)	P(1)–C(15)	1.815(20)
C(1)–C(2)	1.258(27)	P(1)–C(17)	1.732(25)
C(1)–C(5)	1.528(28)	P(1)–C(19)	1.829(21)
C(2)–C(3)	1.551(26)	P(2)–C(21)	1.850(30)
C(2)–C(4)	1.540(29)	P(2)–C(23)	1.848(45)
C(5)–C(6)	1.328(26)	P(2)–C(25)	1.813(23)
C(5)–C(14)	1.430(24)	C(15)–C(16)	1.563(28)
C(6)–C(7)	1.426(28)	C(17)–C(18)	1.579(33)
C(7)–C(8)	1.367(30)	C(19)–C(20)	1.588(38)
C(8)–C(9)	1.454(35)	C(21)–C(22)	1.332(42)
C(9)–C(10)	1.461(30)	C(23)–C(24)	1.221(70)
C(9)–C(14)	1.387(28)	C(25)–C(26)	1.526(31)
C(10)–C(11)	1.333(41)		

C(1)–Pt–P(1)	93.7(5)	C(11)–C(12)–C(13)	117.4(2.4)
C(1)–Pt–P(2)	90.9(5)	C(12)–C(13)–C(14)	123.1(2.3)
P(2)–Pt–Br	86.9(1)	C(13)–C(14)–C(5)	124.6(1.8)
Br–Pt–P(1)	88.8(1)	C(13)–C(14)–C(9)	115.8(1.8)
P(1)–Pt–P(2)	173.2(2)	C(5)–C(14)–C(9)	119.5(1.8)
Br–Pt–C(1)	175.2(6)	Pt–P(1)–C(15)	117.0(7)
Pt–C(1)–C(2)	124.2(1.7)	Pt–P(1)–C(17)	115.6(8)
Pt–C(1)–C(5)	109.7(1.2)	Pt–P(1)–C(19)	111.3(7)
C(2)–C(1)–C(5)	125.6(1.8)	C(15)–P(1)–C(17)	102.2(1.2)
C(1)–C(2)–C(3)	124.7(2.1)	C(17)–P(1)–C(19)	101.4(1.1)
C(1)–C(2)–C(4)	123.5(1.9)	C(15)–P(1)–C(19)	108.0(1.1)
C(3)–C(2)–C(4)	111.7(1.8)	Pt–P(2)–C(21)	111.3(1.1)
C(1)–C(5)–C(6)	121.0(1.7)	Pt–P(2)–C(23)	112.8(1.2)
C(1)–C(5)–C(14)	121.2(1.6)	Pt–P(2)–C(25)	116.1(8)
C(6)–C(5)–C(14)	117.8(1.8)	C(23)–P(2)–C(21)	104.6(1.9)
C(5)–C(6)–C(7)	124.1(1.9)	C(23)–P(2)–C(25)	106.1(1.5)
C(6)–C(7)–C(8)	120.0(2.1)	C(21)–P(2)–C(25)	105.0(1.4)
C(7)–C(8)–C(9)	116.8(2.0)	P(1)–C(15)–C(16)	116.4(1.6)
C(8)–C(9)–C(10)	115.7(2.3)	P(1)–C(17)–C(18)	118.2(1.7)
C(8)–C(9)–C(14)	121.6(1.9)	P(1)–C(19)–C(20)	110.3(1.6)
C(10)–C(9)–C(14)	122.7(2.5)	P(2)–C(21)–C(22)	117.4(2.1)
C(9)–C(10)–C(11)	115.8(2.6)	P(2)–C(23)–C(24)	123.4(6.3)
C(10)–C(11)–C(12)	125.1(2.1)	P(2)–C(25)–C(26)	118.6(2.0)

not equal at 95.1(6) and 90.8(6)°. The corresponding angles are 93.7(5) and 90.9(5)° in (**3**). Incidentally, despite the α-bulk, we find the geometry around the phosphine P atoms to be similar to that of many such bis(phosphine)platinum(II) compounds, even having one P–C vector essentially in the metal 'square plane' (itself distorted in the present cases).

A particularly interesting consquence of (*i*) is that the C(1)–C(2) (olefinic) bond distances in (**1**) and (**3**) are shorter,† at 1.29(3) and 1.258(27) Å respectively, than in related compounds, *cf.* 1.349(36) Å in *trans*-$[PtCl(CH=CH_2)(PEt_2Ph)_2]$[12] or 1.347(11) Å in *trans*-$[PtBr(CH=CHPh)(PPh_3)_2]$,[13] despite the much larger C(1) substituents in the former compounds. This we rationalise on the basis that the abnormally long Pt–C(1) distances preclude any significant $d\pi$–$p\pi$ overlap of metal and alkenyl π^* orbitals, and further implying that such back-bonding must have been significant in the vinyl, although in the earlier paper[12] this was not claimed. Furthermore, if we accept the widely held view that ligands for which the σ-donor/π-acceptor ratio is high, as here, have a high *trans* influence, we should expect long Pt–Br bonds. This is indeed the case. For (**1**), Pt–Br 2.549(2) Å and for (**3**), Pt–Br 2.537(2) Å; *cf.* 2.501(12) Å in *trans*-$[PtBr(CH=CHPh)(PPh_3)_2]$[13] and 2.428(4) Å in *trans*-$[PtBr_2(PEt_3)_2]$.[14] Other aspects of the molecular geometries are normal.

Experimental

Experiments were performed under argon or nitrogen gases in solvents freshly distilled from appropriate drying agents. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Carbon, hydrogen, and halogen analyses were obtained from the Microanalytical Laboratory, University College Dublin or Canadian Microanalytical Service, Vancouver. Infrared spectra were recorded on Perkin-Elmer 298 or 599 spectrophotometers and ^1H n.m.r. spectra on a Bruker WP 80 Fourier-transform instrument.

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† Neither data set is corrected for absorption, which may produce a small effect on the geometry near the platinum atoms. This feature may be responsible for the apparent short length of the C=C double bonds, though these bonds are within the normal range when the e.s.d.s are taken into account.

Table 5. Atom co-ordinates (× 10^4) for (**1**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt	4 114(1)	1 511(1)	1 335(1)
Br	3 311(4)	2 326(1)	1 167(2)
C(1)	476(3)	830(8)	1 577(21)
C(2)	6 069(24)	702(7)	1 126(18)
C(3)	3 454(23)	551(7)	2 146(17)
C(4)	436(3)	128(9)	275(3)
C(5)	311(4)	−179(11)	329(3)
C(6)	205(4)	−357(10)	236(3)
C(7)	108(4)	−1(10)	176(3)
C(8)	231(3)	322(10)	115(3)
C(9)	252(3)	767(9)	3 023(24)
C(10)	127(4)	439(11)	362(3)
C(11)	228(4)	90(10)	426(3)
C(12)	17(4)	263(12)	249(3)
C(13)	331(3)	917(8)	−1 472(21)
C(14)	298(3)	891(10)	−2 878(25)
C(15)	100(4)	1 629(12)	−112(3)
C(16)	−6(8)	1 333(22)	−78(6)
C(17)	417(3)	1 848(9)	−1 630(25)
C(18)	590(5)	1 800(13)	−163(3)
C(19)	718(3)	2 063(9)	2 872(24)
C(20)	835(5)	1 848(13)	198(3)
C(21)	658(3)	1 236(9)	4 155(323)
C(22)	790(4)	2 409(11)	511(3)
C(23)	439(4)	2 042(11)	426(3)
C(24)	278(4)	1 892(11)	451(3)
P(1)	3 192(7)	1 439(1)	−707(4)
P(2)	5 514(8)	1 691(1)	3 187(5)

Preparation of Platinum(II) *and Palladium*(II) σ-*Alkenyls.*—(*a*) trans-[1-(*Adamant*-1-*yl*)*ethenyl*]*bromobis*(*triethylphosphine*)*platinum*(II), *trans*-[$\mathrm{PtBr\{C(C_{10}H_{15}){=}CH_2\}(PEt_3)_2}$] (**1**). The lithium reagent [1-(adamant-1-yl)ethenyl]lithium (14 $\mathrm{cm^3}$ of a 0.2 mol $\mathrm{dm^{-3}}$ solution in $\mathrm{Et_2O}$; 2.8 mmol) with incipient LiBr was added at room temperature during 1.5 h to a suspension of *cis*-[$\mathrm{PtCl_2(PEt_3)_2}$] (1.157 g, 2.3 mmol) in $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$). The reaction mixture was stirred in refluxing $\mathrm{Et_2O}$ (24 h). The resultant pale yellow suspension was shaken with water and hexane and the organic layers subsequently afforded a yellow paste. This was dissolved in the minimum of hexane and chromatographed on silica using hexane as eluant. The *product*, a white solid, was recrystallised from hexane–diethyl ether affording colourless crystals (0.558 g).

(*b*) trans-*Bromo*[2-*methyl*-1-(*naphth*-1-*yl*)*prop*-1-*enyl*]*bis*(*triethylphosphine*)*platinum*(II), *trans*-[$\mathrm{PtBr\{C(C_{10}H_7){=}CMe_2\}(PEt_3)_2}$] (**3**). The Grignard reagent [2-methyl-1-naphth-1-yl)prop-1-enyl]magnesium chloride (25 $\mathrm{cm^3}$ of a 0.125 mol $\mathrm{dm^{-3}}$ solution in $\mathrm{Et_2O}$; 3.1 mmol) with incipient $\mathrm{MgBr_2}$ (excess) was added dropwise at room temperature to a suspension of *cis*-[$\mathrm{PtCl_2(PEt_3)_2}$] (1.477 g, 2.8 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$). The reaction mixture was stirred (48 h) whence a heavy white precipitate deposited. After removal of the $\mathrm{Et_2O}$ under vacuum the residual pale yellow paste was washed with hexane. The product was extracted into, and recrystallised from, benzene as cream *plates* (1.3 g).

(*c*) trans-*Bromo*(2-*methyl*-1-*phenylprop*-1-*enyl*)*bis*(*triethylphosphine*)*platinum*(II), *trans*-[$\mathrm{PtBr\{C(Ph){=}CMe_2\}(PEt_3)_2}$] (**5**). The lithium reagent (2-methyl-1-phenylprop-1-enyl)lithium (15 $\mathrm{cm^3}$ of a 0.125 mol $\mathrm{dm^{-3}}$ solution in $\mathrm{Et_2O}$; 1.8 mmol) with incipient LiBr was added to a suspension of *cis*-[$\mathrm{PtCl_2(PEt_3)_2}$] (0.6 g, 1.55 mmol) in $\mathrm{Et_2O}$ (25 $\mathrm{cm^3}$) at room temperature during 10 min. The bright yellow suspension was stirred in refluxing $\mathrm{Et_2O}$ (48 h). The $\mathrm{Et_2O}$ was removed and the product shaken with water and benzene. The organic layer subsequently afforded a pasty yellow residue which was washed with cold pentane and recrystallised from $\mathrm{Et_2O}$ to give *colourless plates* (0.527 g).

Table 6. Atom co-ordinates (× 10^4) for (**3**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt	2 331(1)	512	3 029(1)
Br	1 506(2)	1 629(1)	4 212(2)
P(1)	2 251(4)	1 221(3)	1 437(4)
P(2)	2 495(5)	−74(3)	4 715(4)
C(1)	2 918(15)	−464(11)	2 120(14)
C(2)	3 814(16)	643(11)	1 937(15)
C(3)	4 227(19)	−1 457(12)	1 607(20)
C(4)	4 640(17)	−80(12)	2 077(19)
C(5)	2 074(15)	−975(10)	1 869(15)
C(6)	1 266(14)	−1 095(11)	2 650(16)
C(7)	467(17)	−1 572(12)	2 479(19)
C(8)	496(18)	−1 938(12)	1 462(20)
C(9)	1 362(20)	−1 812(11)	606(19)
C(10)	1 373(27)	−2 197(13)	−474(21)
C(11)	2 146(26)	−2 068(14)	−1 273(20)
C(12)	2 916(21)	−1 573(13)	−1 172(19)
C(13)	2 887(20)	−1 221(11)	−135(17)
C(14)	2 122(14)	−1 322(9)	784(14)
C(15)	2 858(20)	819(12)	97(15)
C(16)	2 834(25)	1 322(16)	−969(20)
C(17)	1 065(20)	1 405(12)	1 196(19)
C(18)	488(25)	707(14)	787(26)
C(19)	2 733(19)	2 202(12)	1 538(17)
C(20)	3 829(24)	2 178(15)	2 702(24)
C(21)	3 177(25)	558(22)	5 547(22)
C(22)	4 025(28)	889(19)	4 985(31)
C(23)	1 355(42)	−226(26)	5 661(28)
C(24)	1 081(77)	−339(52)	6 616(96)
C(25)	3 145(21)	−991(14)	4 597(20)
C(26)	3 220(26)	−1 432(18)	5 677(23)

(*d*) trans-*Bromo*(2-*methyl*-1-*phenylprop*-1-*enyl*)*bis*(*triethylphosphine*)*palladium*(II), *trans*-[$\mathrm{PdBr\{C(Ph){=}CMe_2\}(PEt_3)_2}$] (**4**). The lithium reagent (20 $\mathrm{cm^3}$ of 0.148 mol $\mathrm{dm^{-3}}$ solution in $\mathrm{Et_2O}$; 4.44 mmol) with incipient LiBr was added dropwise to a stirred suspension of *trans*-[$\mathrm{PdCl_2(PEt_3)_2}$] (0.8 g, 1.9 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) at −30 °C during 1 h. The reaction mixture was stirred at −30 °C (1 h) and at room temperature (1 h). A heavy white precipitate was deposited from the orange solution. The $\mathrm{Et_2O}$ was removed and the product extracted into benzene and filtered. The concentrated filtrate was diluted with hexane, filtered again, and cooled to −30 °C. A white solid was deposited at −30 °C which was recrystallised from $\mathrm{Et_2O}$ affording colourless *needles* (0.263 g).

(*e*) trans-*Bromo*[2-*methyl*-1-(*naphth*-1-*yl*)*prop*-1-*enyl*]*bis*(*triethylphosphine*)*palladium*(II), *trans*-[$\mathrm{PdBr\{C(C_{10}H_7){=}CMe_2\}(PEt_3)_2}$] (**2**). The Grignard reagent (40 $\mathrm{cm^3}$ of a 0.125 mol $\mathrm{dm^{-3}}$ solution in $\mathrm{Et_2O}$; 5 mmol) and incipient magnesium bromide (excess) were slowly added to a yellow suspension of *trans*-[$\mathrm{PdCl_2(PEt_3)_2}$] (2.065 g, 4.8 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) at −60 °C. The colour changed to deep orange, becoming red upon warming to room temperature. After stirring (4 h) the $\mathrm{Et_2O}$ was removed under vacuum and hexane (50 $\mathrm{cm^3}$) added. The resultant suspension was stirred (15 min), filtered, and the residue extracted with benzene (50 $\mathrm{cm^3}$). The benzene solution was concentrated and the orange residue washed with $\mathrm{Et_2O}$ giving an orange solid. This solid darkened on standing at room temperature but was stable under argon at −10 °C (1.5 g).

Reactions of Platinum(II) σ-*Alkenyls.*—(*a*) trans-[2-(*Adamant*-1-*yl*)-1-N-*methyliminoprop*-2-*enyl*]*bromobis*(*triethylphosphine*)*platinum*(II), *trans*-[$\mathrm{PtBr\{C[C(C_{10}H_{15}){=}CH_2]{=}NMe\}(PEt_3)_2}$]. To a solution of (**1**) (0.082 g, 0.12 mmol) in $\mathrm{Et_2O}$ (15 $\mathrm{cm^3}$) was added methyl isocyanide (0.005 g, 0.12 mmol; 6.7 μl) at room temperature. A small amount of white precipitate was deposited instantly and the reaction mixture was stirred at room temperature (12 h). After filtration the Et$_2$O was removed under vacuum and the remaining white solid washed with cold pentane and recrystallised from Et$_2$O giving *colourless crystals* (0.052 g).

(*b*) trans-*Bromo*(3,3-*dimethyl*-1-N-*methylimino*-2-*phenylprop*-2-*enyl*)*bis*(*triethylphosphine*)*platinum*(II), *trans*-[PtBr{C[C(Ph)=CMe$_2$]=NMe}(PEt$_3$)$_2$]. To an Et$_2$O solution of (**5**) (0.165 g, 0.26 mmol) was added methyl isocyanide (0.0106 g, 0.257 mmol; 4.2 μl) at room temperature. After initial heavy white precipitation a clear solution developed with some red-brown precipitate adhering to the sides of the reaction vessel. The solution was stirred (1 h) and filtered. The filtrate afforded a white solid after removal of the Et$_2$O under vacuum. This was crystallised from pentane giving very pale blue *crystals* (0.15 g).

(*c*) trans-*Bromo*[3,3-*dimethyl*-1-N-*methylimino*-2-(*naphth*-1-*yl*)*prop*-2-*enyl*]*bis*(*triethylphosphine*)*platinum*(II), *trans*-[PtBr{C[C(C$_{10}$H$_7$)=CMe$_2$]=NMe}(PEt$_3$)$_2$]. To a solution of (**3**) (0.151 g, 0.204 mmol) in Et$_2$O (50 cm^3) was added methyl isocyanide (0.0084 g, 0.204 mmol; 11.27 μl). A pale green solid was instantly deposited and the reaction mixture was stirred (5 h) at room temperature. The Et$_2$O solution was filtered and the Et$_2$O removed under vacuum affording a white solid. Crystallisation from pentane gave flaky white crystals (0.098 g).

(*d*) trans-*Bromo*(3-*methyl*-2-*phenylbut*-2-*enoyl*)*bis*(*triethylphosphine*)*platinum*(II), *trans*-[PtBr{C(O)(CPh=CMe$_2$)}(PEt$_3$)$_2$]. A solution of (**5**) (0.210 g, 0.34 mmol) in Et$_2$O (25 cm^3) was subjected to a stream of carbon monoxide for 1 h at room temperature. A deep yellow colour developed instantly. The Et$_2$O was removed under vacuum and the yellow powder residue washed with pentane and crystallised from Et$_2$O giving air stable yellow needles (0.205 g).

X-*Ray Structure Analyses.—Crystal data for* (**1**). C$_{24}$H$_{47}$BrP$_2$Pt, M = 672.6, monoclinic, a = 8.300 0(8), b = 30.168(3), c = 10.875(2) Å, β = 94.472(11)°, U = 2 714 Å^3, Z = 4, D_c = 1.645 g cm^{-3}, D_m = 1.66 g cm^{-3} (by flotation), F(000) = 1 336, space group $P2_1/n$, μ(Mo-K_α) = 65.71 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å.

Measurements. Air-stable rhomb-shaped colourless crystals were obtained from slow evaporation of a diethyl ether solution under dinitrogen. The crystals used for data collection had approximate dimensions 0.45 × 0.4 × 0.2 mm. Preliminary cell constants and lattice type were determined from Weissenberg photographs. The crystal density was determined by flotation in aqueous zinc bromide. Final values of the unit-cell dimensions and the intensities of 5 176 reflections in the range $1.5 \leqslant \theta \leqslant 25°$ were measured using graphite monochromatised Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer with the ω–2θ scan technique. Scan angles for each reflection were calculated from the expression $A + B\tan\theta$ (A = 0.85, B = 0.35°) and a constant aperture setting of 4 mm was used throughout. No correction was made for absorption. The data were reduced by applying Lorentz and polarisation corrections to give 4 176 unique reflections, of which 3 314 were treated as 'observed' [$F \geqslant 5\sigma(F)$] and used in the refinement. The structure was solved in space group $P2_1/n$ by heavy-atom methods and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the platinum, bromine, and phosphorus atoms only, and the final converged value for R is 0.0652. Final bond lengths and angles are given in Table 3, and atomic co-ordinates in Table 5.

Crystal data for (**3**). C$_{26}$H$_{43}$BrP$_2$Pt, M = 670.6, monoclinic, a = 13.772(3), b = 17.264(3), c = 12.061(3) Å, β = 100.8(1)°, U = 2 816.8 Å^3, Z = 4, D_c = 1.63 g cm^{-3}, F(000) = 1 368, space group $P2_1/c$, μ(Mo-K_α) = 62.81 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å.

Measurements. Air-stable needle-shaped pale yellow crystals were obtained from evaporation of an ethanol solution under a dinitrogen atmosphere. The crystal used for data collection had approximate dimensions 0.3 × 0.2 × 0.2 mm. Preliminary cell constants and lattice type were determined from Weissenberg photographs. Final values of the unit-cell constants and the intensities of 6 458 reflections in the range $2 \leqslant \theta \leqslant 23°$ were measured using zirconium filtered Mo-K_α radiation on an Enraf-Nonius CAD-3 diffractometer with ω–2θ scan technique. Scan angles and aperture settings for reach reflection were calculated from the expression $A + B\tan\theta$ (A = 1.20, B = 0.40° and A = 0.8, B = 0.4 mm for the scan angle and aperture respectively). Reflections were measured for six scan cycles, or 10 000 peak counts, whichever was completed sooner. The data were reduced by applying Lorentz and polarisation corrections to give a total of 5 001 reflections of which 2 745 had $F \geqslant 5\sigma(F)$ and were used in refinement. The structure was solved by heavy-atom methods in space group $P2_1/c$ and refined by full-matrix least squares with all non-hydrogen atoms anisotropic to a final R factor of 0.0484. No correction was made for absorption. Final bond lengths and angles are in Table 4, and atomic co-ordinates in Table 6.

For both structures, the programs SHELX, PLUTO, ORTEP,[15] and XANADU were used on the Trinity College DEC-2060 computer for all calculations.

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