Nucleophilic (Michael) Additions to $(Ph_2P)_2C{=}CH_2$ when chelated to Platinum(II) Dichloride or Di-iodide

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Treatment of $[PtCl_2(NCBu^t)_2]$ with $(Ph_2P)_2C{=}CH_2$ (vdpp) in dichloromethane gave $[PtCl_2(vdpp\text{-}PP')]$ (**1a**). Treatment of (**1a**) with a variety of amines or *NN*-dimethylhydrazine in dichloromethane gave the Michael addition products rapidly and in good yields, *viz.* $[PtCl_2\{(Ph_2P)_2CHCH_2NHR\}]$ [R = NMe_2 (**2a**), $CH_2CH{=}CH_2$ (**3**), D-CHMePh (**4**), or $CH_2C_6H_4OMe\text{-}4$ (**5a**)]. Complex (**1a**) is more reactive towards Michael addition than is $[PtMe_2(vdpp\text{-}PP')]$; thus it forms adducts with $H_2NC_6H_4Me\text{-}4$ or $H_2NCH_2CO_2Et$, *i.e.* $[PtCl_2\{(Ph_2P)_2CHCH_2NHC_6H_4Me\text{-}4\}]$ (**7**) or $[PtCl_2\{(Ph_2P)_2CHCH_2NHCH_2CO_2Et\}]$ (**8**). It is also remarkably reactive towards carbon nucleophiles, *e.g.* with 1 equivalent of ethyl acetoacetate or acetylacetone in dichloromethane in the presence of anhydrous sodium carbonate it gave $[PtCl_2\{(Ph_2P)_2CHCH_2CH(COMe)(CO_2Et)\}]$ (**10**) or $[PtCl_2\{(Ph_2P)_2CHCH_2CH(COMe)_2\}]$ (**11**), respectively. On prolonged treatment of (**1a**) with sodium iodide in acetone, acetone added to the vinylidene double bond to give $[PtI_2\{(Ph_2P)_2CHCH_2CH_2COMe\}]$ (**13a**). The di-iodo-complex $[PtI_2(vdpp\text{-}PP')]$ (**1b**) was prepared by treating (**1a**) with $NBu^n{}_4I$ in dichloromethane. Complex (**1b**) reacted with Me_2NNH_2 or amine to give adducts, *e.g.* $[PtI_2\{(Ph_2P)_2CHCH_2NHNMe_2\}]$ (**2b**) or $[PtI_2\{(Ph_2P)_2CHCH_2NHCH_2C_6H_4OMe\text{-}4\}]$ (**5b**), but not with carbon nucleophiles under conditions when the corresponding dichloro-complex (**1a**) underwent Michael addition. Variable-temperature n.m.r. spectroscopy was used to compare the rates of some of these reactions; $^{31}P\text{-}\{^1H\}$, $^1H\text{-}\{^{31}P\}$, and ^1H n.m.r. and i.r. data are given.

We have shown that, on chelation, the vinylidene double bond of $CH_2{=}C(PPh_2)_2$ (vdpp) becomes activated towards nucleophilic or Michael addition. Thus when co-ordinated to a Group 6 metal carbonyl, *e.g.* in a complex of type $[M(CO)_4(vdpp\text{-}PP')]$ (M = Cr, Mo, or W), a range of amines, hydrazines, or carbon nucleophiles add smoothly to the vinylidene double bond in a Michael fashion.[1–5] We have also shown that on co-ordination to $PtMe_2$, *i.e.* in the complex $[PtMe_2(vdpp\text{-}PP')]$, the vinylidene double bond becomes more activated than when co-ordinated to $M(CO)_4$, because platinum(II) is more polarizing than $M(CO)_4$.[6,7] We anticipated that with $[PtCl_2(vdpp\text{-}PP')]$ the vinylidene double bond would be even more reactive towards addition owing to the more electron-withdrawing nature of the $PtCl_2$ moiety, but that nucleophiles such as amines, *etc.* might react preferentially to displace Cl^- from Pt^{II}, rather than add to the double bond. However, we have now studied the behaviour of $[PtCl_2(vdpp\text{-}PP')]$ (**1a**) towards nucleophiles and have found that addition to the vinylidene double bond occurs in preference to displacement of Cl^-; thus a variety of nitrogen and carbon nucleophiles add to the double bond without attacking the platinum centre. We report our results here; some of the results formed part of a preliminary communication.[6]

Results and Discussion

(*i*) *Nitrogen Nucleophiles*.—Treatment of $[PtCl_2(NCBu^t)_2]$ in dichloromethane with vdpp gave the sparingly soluble $[PtCl_2(vdpp\text{-}PP')]$ (**1a**) as a white microcrystalline solid in high (93%) yield. This was characterized by (*i*) satisfactory elemental analyses (C, H, and Cl) (Table 1), (*ii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, which showed a single peak at $\delta(P)$ -31.7 p.p.m., ^1J = 3 244 Hz (Table 2), and (*iii*) the $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, which showed a single peak due to the $C{=}CH_2$ protons at δ 6.25 p.p.m. (Table 2), which in the ^1H n.m.r. spectrum became the AA′ portion of an AA′XX′ ($P_2C{=}CH_2$) spin system (Table 2). All other new compounds gave satisfactory analysis (Table 1) except where stated and were further characterized by n.m.r. data (Table 2).

When a solution of complex (**1a**) in dichloromethane was treated with 1 mol equivalent of *NN*-dimethylhydrazine the solution paled rapidly over 3 min and isolation (see Experimental section) gave a white solid, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of which showed a single peak with platinum satellites; $\delta(P)$ -46.4 p.p.m., ^1J = 3 079 Hz (Table 2). We formulate this complex as the adduct $[PtCl_2\{(Ph_2P)_2CHCH_2NHNMe_2\}]$ (**2a**); the i.r. spectrum showed a weak, sharp band at 3 210 cm^{-1} due to ν(N–H), whilst the band at 1 610 cm^{-1}, due to ν(C=C) in the i.r. spectrum of (**1a**) had disappeared. The far-i.r. spectrum (400—250 cm^{-1}) was virtually the same as for (**1a**) showing that the *cis*-$PtCl_2$ moiety was still present. Most significant were the $^1H\text{-}\{^{31}P\}$ n.m.r. data (Table 2) which showed that the resonance of the vinylidene protons of (**1a**) had disappeared and that a triplet at δ 5.12 and a doublet at 2.53 p.p.m., due to the P_2CH and the P_2CHCH_2 protons of the adduct (**2a**), respectively, were present; both these types of hydrogen were also coupled to phosphorus (data in Table 2).

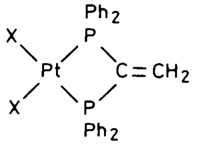
A variety of other amines added to the vinylidene double bond of complex (**1a**) including allylamine, giving (**3**), D-α-methylbenzylamine, giving (**4**), 4-methoxybenzylamine, giving (**5a**), and n-propylamine, giving (**6**), although in the case of (**6**) the product was characterized only by n.m.r. data (Table 2) and was not obtained analytically pure. Preparative details are given in the Experimental section.

We have also found that some less reactive nucleophiles added to (**1a**), whereas previously we had shown that such nucleophiles were insufficiently reactive to add to $[PtMe_2(vdpp\text{-}PP')]$.[6,7] Thus on adding *p*-toluidine in 10-fold excess to a

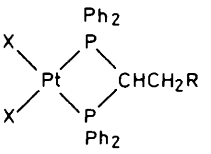
Table 1. Analytical and i.r. spectroscopic data

Complex	Analysis[a]/%				I.r. bands (cm^{-1})[b]
	C	H	N	Halogen	
(**1a**)	51.8 (52.0)	3.7 (3.7)		11.9 (11.9)	1 610m [ν(C=C)], 860s [δ(C=CH_2)]
(**1b**)	36.9 (36.9)	2.4 (2.6)		31.0 (30.3)	1 615m [ν(C=C)], 865s [δ(C=CH_2)]
(**2a**)·CH_2Cl_2[c]	43.2 (43.1)	4.0 (4.0)	3.6 (3.5)	17.4 (17.5)	3 210w [ν(N–H)], 305, 290 [ν(Pt–Cl)]
(**2b**)·0.1CH_2Cl_2[c]	36.7 (36.8)	3.2 (3.3)	2.7 (3.1)	27.5 (27.8)	
(**3**)	48.1 (48.4)	4.1 (4.1)	2.0 (2.0)	10.2 (9.9)	3 265w [ν(N–H)], 310, 290 [ν(Pt–Cl)]
(**4**)[d]	52.0 (52.1)	4.1 (4.2)	2.0 (1.8)	9.2 (9.1)	3 280w [ν(N–H)], 310, 290 [ν(Pt–Cl)]
(**5a**)·0.1CH_2Cl_2[c]	50.6 (50.7)	4.0 (4.1)	1.8 (1.7)	9.8 (9.7)	3 280w [ν(N–H)], 310, 290 [ν(Pt–Cl)]
(**8**)·0.15CH_2Cl_2[c]	46.5 (46.5)	4.0 (4.1)	1.8 (1.8)	10.5 (10.5)	3 285m [ν(N–H)], 307, 287 [ν(Pt–Cl)] 1 735s [ν(C=O)]
(**10**)·0.15CH_2Cl_2[c]	47.9 (47.9)	4.1 (4.1)		10.4 (10.1)	1 720s, 1 740s [ν(C=O)], 315, 300 [ν(Pt–Cl)]
(**11**)	48.6 (48.3)	3.9 (4.0)		9.4 (9.3)	1 750s, 1 760s [ν(C=O)]
(**13a**)	38.6 (38.6)	3.1 (3.1)		28.1 (28.1)	1 715s [ν(C=O)]

[a] Calculated values in parentheses. [b] As Nujol mulls; KBr plates (4 000—400 cm^{-1}), polyethylene plates (500—200 cm^{-1}). [c] The presence of solvent of crystallization was confirmed by ^1H n.m.r. spectroscopy in $CDCl_3$. [d] Molecular weight determination: Found, 769; Calc. for $C_{34}H_{33}Cl_2P_2Pt$, 769.



	X
(**1a**)	Cl
(**1b**)	I



	X	R
(**2a**)	Cl	$NHNMe_2$
(**2b**)	I	$NHNMe_2$
(**3**)	Cl	$NHCH_2CH{=}CH_2$
(**4**)	Cl	D–NHCHMePh
(**5a**)	Cl	$NHCH_2C_6H_4OMe$-4
(**5b**)	I	$NHCH_2C_6H_4OMe$-4
(**6**)	Cl	$NHPr^n$
(**7**)	Cl	NHC_6H_4Me-4
(**8**)	Cl	$NHCH_2CO_2Et$
(**9**)	Cl	SBu^n
(**10**)	Cl	$CH(COMe)(CO_2Et)$
(**11**)	Cl	$CH(COMe)_2$
(**12**)	Cl	$CH(CO_2Et)_2$
(**13a**)	I	CH_2COMe
(**13b**)	Cl	CH_2COMe

solution of (**1a**) in dichloromethane the adduct (**7**) was formed in less than 10 min at 20 °C (^{31}P-{^1H} n.m.r. evidence). This adduct was not obtained pure, being contaminated with about 10% of (**1a**) (n.m.r. evidence), but the characterizing n.m.r. data are given in Table 2. We have found previously that *p*-toluidine does not add to [$PtMe_2$(vdpp-*PP′*)].[6,7] Glycine ethyl ester added to (**1a**) to give the adduct [$PtCl_2\{(Ph_2P)_2CHCH_2NHCH_2CO_2Et\}$] (**8**). However, butanethiol, even in excess, gave only an equilibrium mixture of a reaction product, probably the adduct [$PtCl_2\{(Ph_2P)_2CHCH_2SBu^n\}$] (**9**) and (**1a**) (*ca.* 2:1), as shown by n.m.r. spectroscopy.

In view of the high reactivity of complex (**1a**) towards nucleophiles, attempts were made to follow the progress of additions, using n.m.r. spectroscopy at low temperatures. Remarkably, a solution of (**1a**) (0.02 mol dm^{-3}) in CH_2Cl_2–CD_2Cl_2 reacted quantitatively with 1 mol equivalent of $H_2NC_6H_4OMe$-4 at −80 °C in less than 2 min. Treatment of a similar solution of (**1a**) with Me_2NNH_2 progressed as far as a 1:1 mixture of (**1a**) and (**2a**) in 2 min at −40 °C, *i.e.* the addition was much slower.

(*ii*) *Carbon Nucleophiles.*—When a dichloromethane solution of complex (**1a**) was stirred with 1 mol equivalent of ethyl acetoacetate, in the presence of anhydrous sodium carbonate for 18 h, complete conversion into [$PtCl_2\{(Ph_2P)_2CHCH_2CH(CO_2Et)(COMe)\}$] (**10**) occurred. Owing to the presence of an asymmetric centre, the two phosphorus nuclei are not chemically equivalent and give rise to an AB pattern in the ^{31}P-{^1H} n.m.r. spectrum (see Table 2). Acetylacetone reacted similarly with (**1a**) to give the adduct [$PtCl_2\{(Ph_2P)_2CHCH_2CH(COMe)_2\}$] (**11**). However, when (**1a**) was treated with diethyl malonate and sodium carbonate the hoped for adduct [$PtCl_2\{(Ph_2P)_2CHCH_2CH(CO_2Et)_2\}$] (**12**) was probably formed, as shown by the ^{31}P-{^1H} n.m.r. data (Table 2) but the product was contaminated with some of the starting material (**1a**) and was not obtained pure and not further characterized. Phenylacetylene did not react with (**1a**) either in the presence of sodium carbonate or potassium t-butoxide.

When we attempted to convert the dichloro-complex (**1a**) into the corresponding di-iodide (**1b**) by a standard method of treating it with a solution of sodium iodide in acetone we obtained a yellow solid, the ^1H and ^1H-{^{31}P} n.m.r. spectra of which showed resonances typical of a P_2CHCH_2 system together with resonances which could be assigned to a CH_2COMe moiety. Clearly and somewhat surprisingly, acetone had added to the vinylidene double bond of (**1a**) to give [$PtI_2\{(Ph_2P)_2CHCH_2CH_2COMe\}$] (**13a**). The yield of the isolated complex was typically *ca.* 60% and it gave micro-analytical, i.r., and n.m.r. data confirming the assigned structure. It seemed possible that the di-iodo-complex (**1b**) might be more

Table 2. ^{31}P-{^{1}H}[a] and selected ^{1}H[b] and ^{1}H-{^{31}P}[b] n.m.r. spectroscopic data

Complex	^{31}P-{^{1}H}	^{1}H
(1a)	−31.7 (3 244)	6.25 [AA′XX′,[c] N 63.5, J(PtH) 9]
(1b)	−31.6 (3 023)	6.12 [AA′XX′,[c] N 64.7, J(PtH) 10]
(2a)	−46.4 (3 079)	5.12 [$P_2C\mathit{H}CH_2$, J(HH) 7.4, J(PH) 12.5]
		2.53 [$P_2CHC\mathit{H}_2$, J(HH) 7.4, J(PH) 14.3]
		2.29 (NMe_2)
(2b)	−50.2 (2 886)	5.42 [$P_2C\mathit{H}CH_2$, J(HH) 7.2, J(PH) 12.7, J(PtH) 5.7]
		2.51 [$P_2CHC\mathit{H}_2$, J(HH) 7.2, J(PH) 13.9]
		2.13 (NMe_2)
(3)	−47.9 (3 081)	5.69, 5.04, 5.01 [$CH_2C\mathit{H}^1$=CH^2H^3 respectively (H^1 *trans* H^2)]
		4.49 [$P_2C\mathit{H}CH_2$, J(HH) 8.3, J(PH) 11.8]
		2.89 [$NHC\mathit{H}_2CH$, J(HH) 5.9]
		2.46 [$P_2CHC\mathit{H}_2$, J(HH) 8.3, J(PH) 13.8]
(4)	−47.7, −48.4	4.49 [$P_2C\mathit{H}CH_2$, J(HH) 7.9, J(PH) 11.4, J(PtH) 13.7]
		3.56 [$NHC\mathit{H}MePh$, J(HH) 7.1]
	[AB, ^{1}J(PtP) 3 081, J(PP) 39]	2.34[d] [$P_2CHC\mathit{H}_2$, J(HH) 7.9, J(PH) 13.8]
		1.16 [$NHCH\mathit{Me}Ph$, J(HH) 7.1]
(5a)	−47.7 (3 083)	4.52 [$P_2C\mathit{H}CH_2$, J(HH) 8.0, J(PH) 11.9]
		3.78 (OMe)
		3.35 ($NHC\mathit{H}_2C_6H_4$)
		2.48 [$P_2CHC\mathit{H}_2$, J(HH) 8.0, J(PH) 14.1]
(5b)	−52.4 (2 886)	4.75 [$P_2C\mathit{H}CH_2$, J(HH) 6.6, J(PH) 11.8]
		3.76 (OMe)
		3.27[d] ($NHC\mathit{H}_2C_6H_4$)
		2.48 [$P_2CHC\mathit{H}_2$, J(HH) 6.6, J(PH) 11.4]
(6)	−47.8 (3 083)	
(7)[e]	−48.2 (3 081)	7.02, 6.28 [AA′BB′, 4-C_6H_4]
		3.08 [$P_2CHC\mathit{H}_2$, J(PH) 12.6]
		2.25 ($C_6H_4\mathit{Me}$)
(8)	−48.1 (3 081)	4.61 [$PC\mathit{H}CH_2$, J(HH) 8.5, J(PH) 11.7, J(PtH) 20]
		4.10 [$CO_2C\mathit{H}_2Me$, J(HH) 9.3]
		2.92 ($NHC\mathit{H}_2CO_2$)
		2.46 [$P_2CHC\mathit{H}_2$, J(HH) 8.5, J(PH) 13.2]
		1.19 [$CO_2CH_2\mathit{Me}$, J(HH) 9.3]
(9)	−44.3 (3 083)	
(10)	−45.8, −46.7	4.88 [$P_2C\mathit{H}CH_2$, J(HH) 8.8, J(PH) 11.5, J(PtH) 11.6]
	[J(PtP) 3 099, J(PP) 62]	4.18 [$CO_2C\mathit{H}_2Me$, J(HH) 7.0]
		3.06 [$CH_2C\mathit{H}(COMe)(CO_2Et)$, J(HH) 7.6]
		1.84 (COMe)
		1.67 ($P_2CHC\mathit{H}_2$)
		1.23 ($CO_2CH_2\mathit{Me}$)
(11)	−46.1 (3 088)	4.81 [$P_2C\mathit{H}CH_2$, J(HH) 8.5, J(PH) 11.5]
		3.25 [$CH_2C\mathit{H}(COMe)_2$, J(HH) 7.5]
		1.82 [$CH(CO\mathit{Me})_2$]
		1.65 ($P_2CHC\mathit{H}_2$)
(12)	−50.9 (3 088)	
(13a)	−49.8 (2 899)	5.10 [$P_2CHC\mathit{H}_2$, J(HH) 8.1, J(PH) 19.8]
		2.15 [$P_2CHCH_2C\mathit{H}_2$, J(HH) 6.1]
		1.93 ($CH_2CO\mathit{Me}$)
		1.52 ($P_2CHC\mathit{H}_2CH_2$)
(13b)	−45.7 (3 086)	

[a] Recorded at 40.3 MHz in 20% CD_2Cl_2–CH_2Cl_2. Figures in parentheses are ^{1}J(PtP) in Hz, unless stated otherwise. [b] Recorded at 400 MHz in CD_2Cl_2. [c] Refers to the P_2C=$C\mathit{H}_2$ system. [d] Broadened by additional coupling to NH. [e] The complex was only sparingly soluble; $P_2C\mathit{H}CH_2$ resonances obscured by $CHDCl_2$ peaks.

susceptible to nucleophilic additions than the corresponding dichloro-complex (**1a**). It was therefore important to make some of (**1b**), which we did by treating (**1a**) with an excess of tetra-n-butylammonium iodide in dichloromethane solution (see Experimental section for details and the Tables for characterizing data). However, this di-iodo complex (**1b**) was less reactive towards nucleophilic or Michael addition than the corresponding dichloride (**1a**). For example, although it reacted with 1 mol of equivalent of Me_2NNH_2 or $H_2NCH_2C_6H_4$-OMe-4 in dichloromethane to give [$PtI_2\{(Ph_2P)_2CHCH_2NHNMe_2\}$] (**2b**) or [$PtI_2\{(Ph_2P)_2CHCH_2NHCH_2C_6H_4$-OMe-4$\}$] (**5b**) in good yield, studies of the additions, using variable-temperature ^{31}P-{^{1}H} n.m.r. spectroscopy showed that these reactions were slower than those of the dichloride (**1a**) the hydrazine requiring a temperature of 0 °C to react completely and the amine reacting at −80 °C but requiring 20 min to form a 1 : 1 mixture of (**1b**) and (**5b**) (see Experimental section).

No reaction occurred on treating complex (**1b**) with acetylacetone, ethyl acetoacetate, or diethyl malonate in the presence of anhydrous sodium carbonate. Moreover, when either (**1a**) or (**1b**) was boiled in acetone for 2 d no change occurred, whereas, as discussed above, on treatment with sodium iodide, acetone added to (**1a**) to give (**13a**). We therefore boiled an acetone solution of (**1a**) with either lithium chloride or sodium chloride for 2 d and found in both cases that a new product, characterized by a ^{31}P n.m.r. shift of −45.7 p.p.m. and a ^{1}J(Pt–P) of 3 086 Hz (Table 2), was formed. We were unable to isolate this product in a pure state but the n.m.r. parameters are very similar to those found for compounds (**10**)—(**12**) and we tentatively formulate it as (**13b**). It would appear therefore that the addition of acetone to the co-ordinated vinylidene double bond is promoted by alkali-metal halides, possibly by stabilization of the enolate ion of acetone by the alkali-metal ion.

Experimental

The general methods were the same as in other recent papers from this laboratory.[8]

Preparations.—[$PtCl_2$(vdpp-*PP'*)] (**1a**). Vinylidenebis(diphenylphosphine) (2.0 g, 5.05 mmol) was added to a solution of [$PtCl_2(NCBu^t)_2$] (2.29 g, 5.3 mmol) in dichloromethane (20 cm^3). The mixture was warmed for 15 min, then cooled to 4 °C for 1 h. The white precipitate was filtered off, washed with dichloromethane then with diethyl ether, and dried *in vacuo*. Yield 3.42 g, 93%.

[PtI_2(vdpp-*PP'*)] (**1b**). A solution of tetra-n-butylammonium iodide (0.443 g, 1.2 mmol) in dichloromethane (7 cm^3) was added to a solution of complex (**1a**) (0.20 g, 0.302 mmol) in dichloromethane (20 cm^3). The resultant mixture was then stirred for 30 min and the volume reduced to *ca.* 7 cm^3. The product was filtered off and recrystallized from dichloromethane–methanol. It formed yellow microcrystals. Yield 0.22 g, 88%.

Complex (**2a**). A solution of complex (**1a**) (0.20 g, 0.302 mmol) in dichloromethane (15 cm^3) was treated with *N,N*-dimethylhydrazine (24 μl, 0.306 mmol). After 3 min a pale yellow solution had formed. This was then evaporated to low volume and the required product precipitated with diethyl ether. Yield 0.21 g, 86%.

The following complexes were prepared similarly.

(**3**), *Using allylamine.* White microcrystals formed from dichloromethane–diethyl ether. Yield 74%.

(**4**), *Using* D-α-*methylbenzylamine.* White microcrystals formed from dichloromethane–diethyl ether. Yield 90%.

(**5a**), *Using* 4-*methoxybenzylamine.* Pale yellow microcrystals formed from dichloromethane–diethyl ether. Yield 88%.

(**7**), *Using* p-*toluidine.* A 10-fold excess of the amine was necessary to cause complete conversion. The product formed white microcrystals from dichloromethane–diethyl ether but n.m.r. spectroscopy showed that it was contaminated with (**1a**), *i.e.* some dissociation occurred on isolation and the adduct was not obtained pure (see Discussion).

(**2b**). This was prepared from complex (**1b**), in an analogous manner to (**2a**), except that methanol was used to precipitate the product instead of diethyl ether. It formed yellow microcrystals. Yield 90%.

(**5b**). This was prepared from complex (**1b**), in an analogous manner to (**5a**). It formed yellow rhombs from dichloromethane–diethyl ether. Yield 79%.

(**8**). A solution of glycine ethyl ester was prepared by neutralization of a solution of the hydrochloride (0.433 g, 3.2 mmol) with KOH (0.180 g, 3.2 mmol) in methanol. An aliquot (2 cm^3, containing 0.7 mmol of the glycine ester) was added to a solution of complex (**1a**) (0.20 g, 0.302 mmol) in dichloromethane (25 cm^3) and the resultant mixture stirred for 82 h at 20 °C. The solvent volume was then reduced *in vacuo* to give the required product as white microcrystals. Yield 0.22 g, 95%.

(**10**). A solution of complex (**1a**) (0.20 g, 0.302 mmol) and ethyl acetoacetate (38 μl, 0.31 mmol) was stirred in the presence of anhydrous sodium carbonate (15 mg) for 17 h. The mixture was then filtered and the filtrate evaporated to dryness. The residue was triturated with diethyl ether and the resultant solid recrystallized from dichloromethane–diethyl ether as white microcrystals. Yield 0.225 g, 86%.

(**11**). A solution of complex (**1a**) (0.20 g, 0.302 mmol) and acetylacetone (31 μl, 0.302 mmol) in dichloromethane (15 cm^3) was stirred in the presence of $KOBu^t$ (1 mg) for 17 h. The mixture was then filtered and the product isolated from the filtrate by evaporation. It formed white microcrystals from dichloromethane–cyclohexane. Yield 0.18 g, 80%.

(**13a**). A suspension of complex (**1a**) (1.45 g, 2.2 mmol) in acetone (50 cm^3) was treated with sodium iodide (3.3 g, 22 mmol) and the resultant mixture heated under reflux for 40 h. The solvent was then removed *in vacuo*, the residue washed with water, dried, and recrystallized from dichloromethane–toluene as pale yellow microcrystals. Yield 1.25 g, 63%.

Monitoring of Michael additions by $^{31}P-\{^1H\}$ *N.M.R. Spectroscopy.*—The following examples are typical. A solution of complex (**1a**) (0.02 g, 0.03 mmol) in CH_2Cl_2–CD_2CL_2 (1.5 cm^3) in a n.m.r. tube (outside diameter 10 mm) was cooled to −80 °C in the probe of a JEOL FX-100 n.m.r. spectrometer. The appropriate hydrazine or amine as a 10% solution in dichloromethane was then added in equimolar amount by syringe and spectra taken at intervals. The temperature was increased stepwise and further spectra taken until reaction occurred. For Me_2NNH_2 this was at −40 °C ($t_{\frac{1}{2}}$ 6 min), for 4-$MeOC_6H_4CH_2NH_2$ at −80 °C ($t_{\frac{1}{2}}$ 2 min). These reactions were repeated using the di-iodo-complex (**1b**) (0.02 g, 0.024 mmol) and the hydrazine or amine (0.024 mmol). With Me_2NNH_2 a very slow reaction commenced at −50 °C, which did not go to completion until the mixture was warmed to 0 °C. With 4-$MeOC_6H_4CH_2NH_2$ a slow reaction occurred at −80 °C ($t_{\frac{1}{2}}$ 18 min).

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References

1 G. R. Cooper, D. M. McEwan, and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **76**, L165.
2 G. R. Cooper, F. S. M. Hassan, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 614.
3 G. R. Cooper, D. M. McEwan, and B. L. Shaw, *Inorg. Chim. Acta*, 1986, **122**, 207.
4 F. S. M. Hassan, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 89.
5 A. M. Herring, S. M. Koskimes, and B. L. Shaw, *J. Organomet. Chem.*, 1988, **338**, 13.
6 X. L. R. Fontaine, F. S. M. Hassan, S. J. Higgins, G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 1635.
7 F. S. M. Hassan, S. J. Higgins, G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 3011.
8 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.

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