Reactions involving Transition Metals. Part XI.[1] Reactions of Nucleophiles with Dieneplatinum Complexes

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The reactions of the complexes [Pt(diene)Cl_2] (diene = norbornadiene or dicyclopentadiene) with the nucleophiles OPr^{i-}, NH_2Ph, SPh^-, and SCN^- have been investigated. The dicyclopentadiene complex undergoes attack at the diene in each case and the S-nucleophiles also give substitution at platinum. Only the latter reaction occurs with the norbornadiene complexes and S-nucleophiles, but attack on the organic ligand is found with OPr^{i-} and NH_2Ph. The reactions of these products with neutral uni- and bi-dentate ligands usually leads to bridge-splitting reactions, but in some cases the norbornenyl derivatives undergo rearrangement to nortricyclene systems. The reaction of the alkenyl complexes with a further nucleophile (OMe^- or $NHPh^-$) to give doubly σ-bonded alkyleneplatinum complexes is described.

NUCLEOPHILIC attack on dienes co-ordinated to palladium or platinum has been much studied in recent years,[2-13] and it is now well established that the nucleophile attacks one double bond of the diene in the *exo* position (*trans* to the metal) although an example of *endo* attack has been reported recently.[14] In this paper we report an extension of the range of nucleophiles to include thio-compounds, the reactions of the products with neutral ligands, and the introduction of a second nucleophile by attack at the remaining double bond. Some of these results have already been briefly communicated.[5] Our results are summarised in Scheme 1.

RESULTS

Reactions of Nucleophiles with [Pt(diene)Cl_2].—Complexes (I; diene = norbornadiene, C_7H_8, or dicyclopentadiene, $C_{10}H_{12}$) reacted with n-propoxide ion at room temperature, but heating to 65 °C was required to obtain reaction with isopropoxide ion, when (II; alkenyl = C_7H_8 or $C_{10}H_{12}$, R = OPr^i, X = Cl) were obtained, the n.m.r. and i.r. spectra of which demonstrate conventional structures (Tables 1—3). The tricyclodecenyl † complex showed two n.m.r. signals for the $(CH_3)_2CHO$ protons which coalesced at 40 °C, suggesting hindered rotation. No reaction of (I) occurred with t-butoxide ion at 65 °C but a trace of adduct was obtained at 80 °C from (I; diene = $C_{10}H_{12}$).

Reaction of (I) with aniline in the presence of a base gave insoluble products (II; alkenyl = C_7H_8 or $C_{10}H_{12}$, R = NHPh, X = Cl), the i.r. spectra of which indicate the presence of terminal Pt–Cl bonds and co-ordinated tertiary amine groups [ν(N–H) at 3 230—3 300 cm^{-1}], showing that polymerisation occurs by amine-group bridging, as was suggested by Palumbo *et al.*[10] during the course of our work. These workers were apparently unable to obtain amino-derivatives from complexes (I), but isolated similar compounds from vinylcyclohexene and hexa-1,5-diene complexes.[10] When two molar equivalents of aniline were used, the bridge-cleaved product (III; alkenyl = $C_{10}H_{12}$, R = NHPh, X = Cl, L = NH_2Ph) was obtained [ν(>NH) at 3 260 cm^{-1}, ν($PhNH_2$–Pt) at 3 380 cm^{-1}]. In the absence of triethylamine, the norbornadiene complex did not react with aniline, but (I; diene = $C_{10}H_{12}$) gave (IV) which contains a quaternary amino-group [ν(N–H) at 2 200—3 100 cm^{-1}] and terminal Pt–Cl groups. On treatment with a strong base, (IV) lost the elements of hydrogen chloride to give (III).

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† Tricyclodecenyl = $C_{10}H_{12}$ = *endo*-5σ,2π-*exo*-6-(substituted)-3a,4,7,7a-tetrahydro-*endo*-methanoindenyl.

[1] Part X, C. E. Betts, R. N. Haszeldine, and R. V. Parish, *J.C.S. Dalton*, 1975, 2218.

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[3] J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5135.

[4] R. G. Schultz, *J. Organometallic Chem.*, 1966, **6**, 435.

[5] R. N. Haszeldine, R. V. Parish, and D. W. Robbins, *J. Organometallic Chem.*, 1970, **23**, C33.

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[8] M. N. S. Hill, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1971, 2341.

[9] D. A. White, *J. Chem. Soc.* (*A*), 1971, 145.

[10] R. Palumbo, A. de Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, 1969, **91**, 3874.

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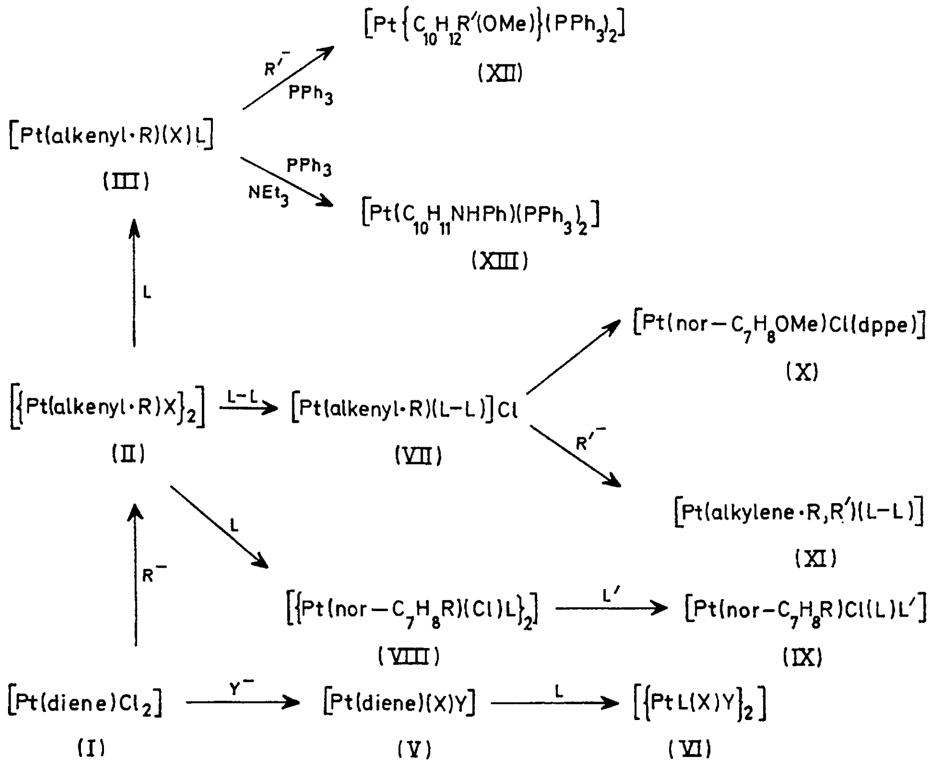
[12] J. Tsuji and H. Takahashi, *J. Amer. Chem. Soc.*, 1965, **87**, 3275.

[13] B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc.* (*A*), 1968, 1993.

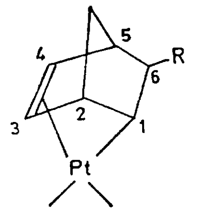
[14] A. Segnitz, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1973, 698.



SCHEME 1

TABLE 1

N.m.r. data for norbornenyl complexes [figures in parentheses are ${}^2J$(Pt–H)/Hz]

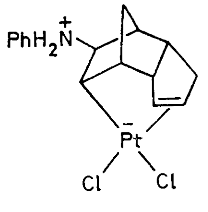


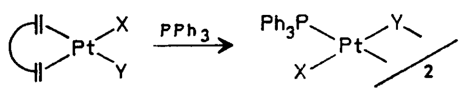
	τ_3	τ_4	τ_6	τ_2	τ_5	τ_1	τ_R
$[\{Pt(C_7H_8OMe)Cl\}_2]$	4.57 (108)	5.12 (*ca.* 100)	5.91	6.66	7.43	7.92 (*ca.* 105)	6.79
$[\{Pt(C_7H_8OPr^i)Cl\}_2]$	4.60 (105)	5.14 (*ca.* 100)	5.74	6.66	7.54	7.96 (*ca.* 120)	6.39 8.91
$[Pt(C_7H_8OMe)Cl(py)]$	4.74 (92)	5.56 (89)	5.93	6.64	7.47	7.75 (*ca.* 115)	6.77
$[Pt(C_7H_8OPr^i)Cl(py)]$	4.70 (96)	5.50 (80)	5.71	6.60	7.52	7.82 (*ca.* 95)	6.31 8.86, 8.88
$[Pt(C_7H_8OMe)(dppe)]Cl$	4.05	4.47	5.76	6.82 [a]	7.42	7.80	6.92 [a]

[a] The corresponding signals in $[Pt(C_7H_8OMe)Cl(dppe)]$ occur at τ 6.25 and 6.82.

Complexes (I; diene = C_7H_8 or cyclo-octa-1,5-diene, C_8H_{12}) reacted with two molar equivalents of thiocyanate or benzenethiolate ion to give (V; X = Y = SCN or SPh) by simple replacement of chloride. The i.r. and n.m.r. spectra (Tables 4 and 5) indicate that the diene ligands are intact and that the thiocyanato-groups are S-bonded. These products reacted with one molar equivalent of triphenylphosphine with loss of diene to give the dimers (VI; X = Y = SCN or SPh, L = PPh_3). The intermediate half-substituted products were also isolated (V; diene = C_7H_8, X = Cl, Y = SPh) and (VI; X = Cl, Y = SPh). The n.m.r. spectrum of the former did not indicate the expected non-equivalence of the vinylic protons. Since the complex is a non-conductor in nitromethane, symmetrical structures

(IV)

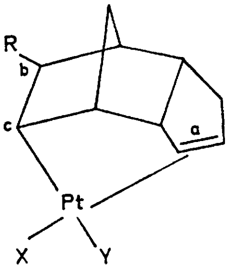




(V) (VI)

TABLE 2

N.m.r. data for tricyclodecenyl complexes. Values of ^2J(Pt–H)/Hz are given in parentheses



R	X	Y	τ_a		τ_b	τ_c	τ_R
OMe	Cl	Cl	4.83 (*ca.* 100)	4.83 (*ca.* 110)	6.51	7.81	6.78
OMe	Cl	py	5.10 (100)	5.46 (80)	6.40	7.66	6.61
OMe	py	Cl	3.93 (75)	4.50 (90)	6.33	7.76	6.82
OMe	PPh_3	Cl	3.30 (60)	3.30 (70)	6.68	7.79 (*ca.* 100)	7.21
OPr^i	Cl	Cl	4.84 (95)	4.90 (110)	6.36	7.91 (*ca.* 100)	6.36, 8.90, 8.92
OPr^i	Cl	py	5.14 (*ca.* 100)	5.51 (*ca.* 95)			8.87
OPr^i	py	Cl	3.96 (*ca.* 80)	4.54 (*ca.* 95)			8.91
OPr^i	PPh_3	Cl	3.24 (*ca.* 50)	3.24 (*ca.* 80)	6.18	7.87	6.18, 9.05, 9.25
NHPh	NHPh	Cl	4.36 (*ca.* 70)	4.70 (*ca.* 110)	6.23	7.90 (*ca.* 110)	2.69, 6.31
NHPh	Cl	py	4.59 (96)	5.38 (*ca.* 90)	5.80	7.92	2.92, 3.43, 6.24
NHPh	py	Cl	3.88 (80)	4.47 (95)		7.75	2.92, 3.43, 6.24
NHPh	PPh_3	Cl	3.25	3.25	6.43	7.82 (125)	2.97, 3.46, 3.80, 7.25
SCN	PPh_3	SCN	3.32	3.49	6.67	7.79 (*ca.* 100)	
SPh	SPh	SPh	4.78	5.03	6.56	8.00	

of the type $[(H_8C_7)Pt(\mu\text{-}SPh)_2Pt(C_7H_8)]Cl_2$ can be discounted. The n.m.r. data presumably indicate rapid exchange of chloride and benzenethiolate ligands, and the chemical shift and coupling constants must be average values.

TABLE 3

Far-i.r. data (cm^{-1}) for chloro-complexes

	ν(Pt–Cl)	Other
$[\{Pt(C_{10}H_{12}OMe)Cl\}_2]$	290s, 214m	349mw, 329mw, 235mw
$[\{Pt(C_{10}H_{12}OPr^i)Cl\}_2]$	291s, 212m	359m, 345m, 270m
$[\{Pt(C_7H_8OMe)Cl\}_2]$	287m, 207m	339m, 310w, 271mw, 258mw
$[\{Pt(C_7H_8OPr^i)Cl\}_2]$	276m, 201m	390w, 337mw, 231mw
$[Pt(C_{10}H_{12}NH_2Ph)Cl_2]$	294s, 231vs	399s, 349m, 267m, 238 (sh)
$[\{Pt(C_{10}H_{12}NHPh)Cl\}_n]$	259s	385s, 350mw, 315w, 238mw
$[Pt(C_{10}H_{12})Cl(SPh)]$ $[\{Pt(C_{10}H_{12}SPh)Cl\}_2]$	332ms, 323ms 306ms, 240ms	393vw, 349w, 275w
$[Pt(C_{10}H_{12}OMe)Cl(py)]$	309s	350mw, 329w, 242m
$[Pt(C_{10}H_{12}OPr^i)Cl(py)]$	310s	357mw, 348mw, 282mw
$[Pt(C_{10}H_{12}NHPh)Cl(py)]$	311ms	356mw, 285m
$[Pt(C_7H_8OMe)Cl(py)]$	305s	395ms, 265ms
$[Pt(C_7H_8OPr^i)Cl(py)]$	279m, 249m	
$[Pt(C_7H_8NHPh)Cl(py)]$	296ms, 280m	400mw, 330mw
$[Pt(C_{10}H_{12}OMe)Cl(PPh_3)]$	264s	374w, 330w, 287w, 237vw
$[Pt(C_{10}H_{12}OPr^i)Cl(PPh_3)]$	270s, 255 (sh)	
$[Pt(C_{10}H_{12}NHPh)Cl(PPh_3)]$	270s	370w, 330w, 310w, 250w, 240w
$[\{Pt(C_7H_8OMe)Cl(PPh_3)\}_2]$	291m, 269m	342w
$[\{Pt(C_7H_8OPr^i)Cl(PPh_3)\}_2]$	285m, 246m	
$[\{Pt(C_7H_8NHPh)Cl(PPh_3)\}_2]$	272m, 245mw	
$[Pt(C_7H_8OMe)Cl(PPh_3)_2]$	300mw, 265m	
$[Pt(C_7H_8OMe)Cl(PMePh_2)(PPh_3)]$	290w, 260m	
$[Pt(C_7H_8OMe)Cl(PEt_3)_2]$	249s	241(sh), 227ms
$[Pt(C_7H_8OPr^i)Cl(PPh_3)_2]$	252m, 246m	

TABLE 4

N.m.r. data for dieneplatinum complexes

Complex	τ(=C*H*–)	^2J(Pt–H)/ Hz	Other
$[Pt(C_8H_{12})(SPh)_2]$	5.37	58	7.3—8.3
$[Pt(C_8H_{12}(SCN)_2]$	4.52	52	7.2—7.6
$[Pt(C_7H_8)(SPh_2]$ (XIII)	5.97	54	6.14, 8.60
$[Pt(C_7H_8)Cl(SPh)]$ (XII)	5.30	64	5.87, 8.41

TABLE 5

C≡N Stretching wavenumbers (cm^{-1}) for thiocyanate derivatives

Complex	
$[Pt(C_7H_8)(SCN)_2]$ (VII)	2 137s
$[Pt(C_8H_{12})(SCN)_2]$	2 126s
$[\{Pt(C_{10}H_{12}NCS)(SCN)\}_2]$ (IX)	2 156s, 2 112m, 2 054s
$[\{Pt(C_{10}H_{12}OMe)(SCN)\}_2]$	2 156s
$[Pt(C_{10}H_{12}NCS)(PPh_3)(SCN)]$ (X)	2 158 (sh), 2 152s, 2 099s, 2 078 (sh)
$[Pt(C_{10}H_{12}\cdot H_2NC_6H_4Me\text{-}p)(SCN)_2]$ (XI)	2 125s, 2 105s

Complex (I; diene = $C_{10}H_{12}$) reacted with two molar equivalents of thiocyanate or benzenethiolate ion to give products in which chloride-substitution and nucleophilic attack have both occurred (II; alkenyl = $C_{10}H_{12}$, R = NCS or SPh, X = SCN or SPh). Comparison of the i.r. spectra of the thiocyanato-complex with that of $[\{Pt(C_{10}H_{12}OMe)(SCN)\}_2]$ showed that the organic substituent is bound through nitrogen, C–NCS. This complex reacted with PPh_3 without loss of organic ligand to give (III; alkenyl = $C_{10}H_{12}$, R = NCS, X = SCN). Curiously, the attempted bridge-splitting reaction with *p*-toluidine led to a product of type (IV) in which the organic isothiocyanato-group had been displaced, $[\overset{-}{Pt}(C_{10}H_{12}\cdot H_2\overset{+}{N}C_6H_4Me\text{-}p)(SCN)_2]$. Nucleophilic displacement of thiocyanate has been reported in other organic systems,[15] and similar

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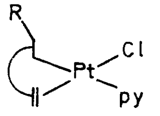
[15] C. G. Swain and D. C. Dittmer, *J. Amer. Chem. Soc.*, 1955, **77**, 3924; S. Bodforss and S. Ahrland, *Acta Chem. Scand.*, 1951, **5**, 227; A. Hantsch and A. Burawoy, *Ber. Deutsch Chem. Gesellschaft*, 1930, **63**, 1181.

mobility is required in thiocyanate–isothiocyanate isomerisation.[16] The benzenethiolate derivative did not react with PPh_3.

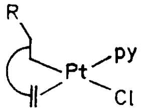
With only one molar equivalent of benzenethiolate ion, (I; diene = $C_{10}H_{12}$) gave a mixture of (II; alkenyl = $C_{10}H_{12}$, R = SPh, X = Cl) and (V; diene = $C_{10}H_{12}$, X = Cl, Y = SPh). The integration of the vinylic-proton region of the n.m.r. spectrum (*ca.* 2.8 protons) suggested that (II) formed *ca.* 60% of the product.

Reactions of Dimeric Complexes with Neutral Ligands.—Complexes (II; alkenyl = $C_{10}H_{12}$, X = Cl) reacted with pyridine or tertiary phosphines by bridge cleavage to give (III; alkenyl = $C_{10}H_{12}$, X = Cl, R = OMe, OPr^i, or NHPh, L = py or PPh_3; and X = SCN, R = NCS, L = PPh_3). The far-i.r. spectra of the chloro(phosphine) complexes show that Cl is *trans* to the Pt–C σ bond, which is confirmed by the downfield shift of the vinylic resonances in the n.m.r. spectra. The methyl signals of the methoxy- and isopropoxy-groups were shifted upfield by the shielding effect of the bulky phosphine ligand in the *cis* position. The latter resonance occurred as two well resolved doublets, 0.2 p.p.m. apart; on warming the solution, these signals became closer but had not completely merged even at 120 °C, indicating restricted rotation with a much higher energy barrier than for the chloro-bridged dimer. Steric interactions with the phosphine were clearly evident on examination of a molecular model.

In the n.m.r. spectra of the pyridine derivatives, several sets of signals were duplicated, the most striking being those of the α-hydrogens of pyridine, the vinylic hydrogens of the tricyclodecenyl group, and those of the methoxy-group. On the basis of the high *trans* influence of the Pt–C σ bond, which would result in less donation from a pyridine in the *trans* position than the *cis* position, we assign the higher-field H_α pyridine resonance to isomer (i). Similar differences in chemical shift have been observed in the reaction of *trans*-[$Pt(C_2H_4)Cl_2(py)$] with pyridine.[17] The resonances of the vinylic protons of the two isomers were well separated and differentiated by their relative intensities. If the above assignment is correct, replacement of chloride by pyridine *trans* to the double bond gives rise to a downfield shift of *ca.* 1 p.p.m. The relative intensities of the two sets of signals in the spectrum of the methoxy-compound did not change when the solution was kept for several days, indicating either that the isomers do not interconvert or that they are already at equilibrium. The three complexes, however, gave different ratios of concentrations of the two isomers. The i.r. data are also consistent with the presence of both isomers.



(i)



(ii)

diene = $C_{10}H_{12}$

R	(i):(ii)
OMe	*ca.* 2 : 1
OPr^i	*ca.* 2 : 2
NHPh	*ca.* 2 : 3

Similar reactions occurred with the bidentate ligands 2,2′-bipyridyl (bipy) and 1,2-bis(diphenylphosphino)ethane (dppe) to give the 1 : 1 electrolytes (VII; alkenyl = $C_{10}H_{12}$). Conductimetric titration of (II) with bipy in nitromethane gave a sharp end-point after the addition of 2 mol of bipy per mol of dimer.

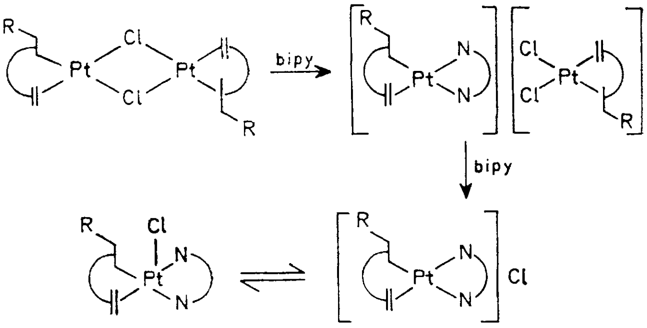
The norbornenyl * complexes reacted similarly with py and bipy. The i.r. spectra of the py derivatives showed the presence of both isomers but the n.m.r. spectra indicated that only 10—15% of isomer (ii) was present. The conductivity of the bipy complex (VII; alkenyl·R = C_7H_8·OMe, X = Cl) in nitromethane and in dichloromethane was lower than expected for a 1 : 1 electrolyte (*cf.* Table 6), suggesting some association. The i.r. spectra of the solid complexes showed bands at 210—220 cm^{-1}, possibly indicative of weak Pt–Cl bonds.

TABLE 6

Molar conductivities (S cm^2 mol^{-1}) for 10^{-3} mol dm^{-3} solutions, and Pt–Cl stretching wavenumbers (cm^{-1}) for 2,2′-bipyridyl and 1,2-bis(diphenylphosphino)ethane complexes

	λ		
Complex	$MeNO_2$	CH_2Cl_2	ν(Pt–Cl)
[$Pt(C_7H_8OMe)Cl(bipy)$]	50.4	2.5	215ms
[$Pt(C_{10}H_{12}OMe)Cl(bipy)$]	93.0	12.6	221s
[$Pt(C_{10}H_{12}NHPh)Cl(bipy)$]	86.5	10.9	210m
[$Pt(C_7H_8OMe)(bipy)$][BPh_4]	78.9		
[$Pt(C_{10}H_{12}OMe)(dppe)$]Cl	74.6	55.1	

Typical values for 1 : 1 electrolytes are 75—90 S cm^2 mol^{-1} for $MeNO_2$ and 18—40 S cm^2 mol^{-1} for CH_2Cl_2.



SCHEME 2

When (II; alkenyl·R = C_7H_8·OMe, X = Cl) in nitromethane was treated with bipy, the conductivity increased linearly during addition of one molar equivalent but rose much less rapidly thereafter, becoming constant after the addition of two molar equivalents. In dichloromethane, the conductance rose to a maximum after the addition of 1 mol of bipy (corresponding to a molar conductance of 21.8 S cm^2 mol^{-1}) and reached a constant low value after the addition of 2 mol. These data are consistent with the reactions shown in Scheme 2, in which attack of bipy initially gives a 1 : 1 electrolyte by unsymmetrical bridge cleavage. Further reaction gives the final complex which may be partially or almost completely associated. Similar

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* Norbornenyl = C_7H_8 = *endo*-5σ,2π-*exo*-6-(substituted)-bicyclo[2.2.1]hept-2-enyl.

[16] G. Caprioli and A. Illiceto, *Ricerca sci.*, 1956, **26**, 2714; A. Fava and A. Illiceto, *ibid.*, 1955, **25**, 54; O. Mumm and H. Richter, *Ber. Deutsch Chem. Gesellschaft*, 1940, **73**, 843; O. Billeter, *Helv. Chim. Acta*, 1925, **8**, 377.

[17] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, 1968, **90**, 4175.

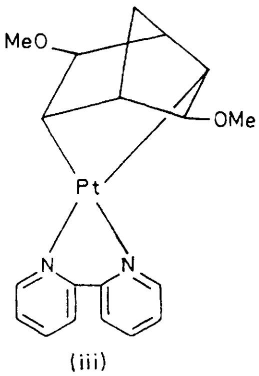
results were reported[18] for tricyclodecenyl complexes during the course of our work.

Complexes (II; alkenyl = C_7H_8) reacted with two molar equivalents of PPh_3 to give dimeric products, (VIII), the i.r. spectra of which indicated the retention of the $Pt-Cl_2-Pt$ bridging system. In addition, bands were found at *ca.* 810 cm^{-1} indicating that the organic ligand had undergone rearrangement to a nortricyclenyl[*] system.[19] This was confirmed by the n.m.r. spectra which showed no resonances in the vinylic region, τ 3—5.5, but had a series of bands in the range τ 8—9.5 similar to those reported previously.[7]

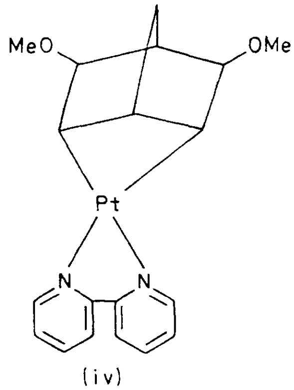
These products reacted with a further two molar equivalents of a tertiary phosphine to give monomeric products by bridge-cleavage, (IX). The far-i.r. spectra of these complexes all gave at least two bands in the Pt–Cl region. For the methoxy-complexes these could be unambiguously assigned to chloride *trans* to a phosphine (290—300 cm^{-1}) or *trans* to the σ-bonded nortricyclenyl groups (260—265 cm^{-1}), indicating the presence of both *trans* and *cis* isomers with the former probably predominating. In the other two cases, all the bands lay in the lower region, suggesting that these are *trans* isomers; the appearance of more than one band must be attributed to solid-state effects. These structures are supported by the n.m.r. spectra. The bis(triethylphosphine) complex showed single, sharply defined, resonances for the CH_3O and MeOC*H* protons, and the coupling pattern of the P-ethyl groups was characteristic of a *trans*-bis(phosphine) complex. In the spectrum of the corresponding bis(triphenylphosphine) complex both the CH_3O and MeOC*H* signals were duplicated and in each case the signal to higher field had slightly the higher intensity (*ca.* 0.8 : 1). On the assumption that shielding is due mainly to the *cis* ligands, the higher-field resonances may be assigned to the *trans* isomer. The mixed complex, (IX; L = PPh_3, L′ = PEt_3), showed further duplication of these signals, suggesting the presence of different conformers of each isomer.

A dichloromethane solution of $[\{Pt(C_7H_8OMe)Cl\}_2]$ reacted with dppe in two stages. When reaction was stopped after a few minutes by precipitating with hexane, the product consisted primarily of the ionic substitution derivative (VII). When the reaction was allowed to continue for several hours, the organic ligand rearranged and a non-ionic product, (X), was obtained. The reaction could be readily followed by monitoring the n.m.r. spectrum; the disappearance of the vinyl-proton resonance and the growth of a second methoxy-group signal were clearly visible. Similarly, the electrical conductivity of a solution of the original dimer increased rapidly on addition of dppe (two molar equivalents) and then declined slowly as the rearrangement proceeded.

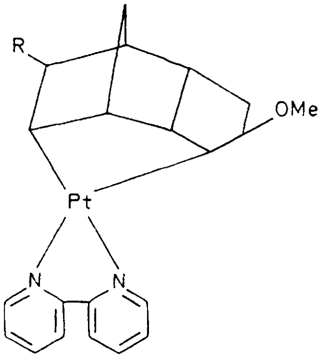
Ligand-displacement Reactions.—Complexes (III; alkenyl = $C_{10}H_{12}$, X = Cl, L = py) reacted with PPh_3 with loss of pyridine to give (III; L = PPh_3). Although the pyridine complex was a mixture of isomers, only one form of each of the triphenylphosphine complexes was detected, as in the cleavage reaction of $[\{Pt(C_{10}H_{12}OMe)Cl\}_2]$. The reaction of the corresponding norbornenyl complex also led to substitution of PPh_3 for py, but this was immediately followed by rearrangement to a nortricyclenyl derivative identical to that obtained by reaction of (II) with PPh_3. The same product was also obtained by treating the bipyridyl complex (VII; alkenyl·R = $C_{10}H_{12}$·OMe) with PPh_3.



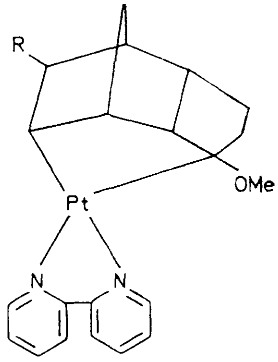
(iii)



(iv)



(v)



(vi)

Introduction of a Second Nucleophile.—The bipyridyl complexes (VII) reacted at room temperature with sodium methoxide to give bright red air-stable (XI; L–L = bipy), in which the double bond of the alkenyl group had undergone nucleophilic attack forming a second Pt–C σ bond. The ^1H n.m.r. spectrum of the norbornylene[†] complex (XI; alkylene = C_7H_8) (Table 7) showed single sharp resonances for the CH_3O, CH_2, CH_3OCH, and *C*HPt groups, indicating a highly symmetrical structure which can only be (iii). The alternative isomer (iv) would be expected to show marked inequivalence of the bridgehead protons, as in the complexes (III; alkenyl = C_7H_8) and (VII; alkenyl = C_7H_8, L–L = dppe). No signals appeared in the vinylic region.

Two isomers (v) and (vi) are also possible for disubstituted tricyclodecylene[‡] complexes (XII; alkylene = $C_{10}H_{12}$). From an examination of molecular models, neither isomer appears to have significantly less steric strain. In each case, only one isomer appears to have been formed, tentatively assigned structure (v) on the basis of the doublet structure (separation 4 Hz) of the lower-field (τ 5.75) CH_3OCH resonance, which suggests coupling to the *cis* proton of a CH_2 group. The two different MeO groups in the dimethoxy-compound were just resolved (by 0.03

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[*] Nortricyclenyl = nor-C_7H_8 = *endo*-3σ-*exo*-5-(substituted)-tricyclo[2.2.1.0]heptyl.

[†] Norbornylene = *endo*-3σ,5σ-*exo*-2,5-(disubstituted)-bicyclo-[2.2.1]hept-2-ene.

[‡] Tricyclodecylene = *endo*-3σ,6-*exo*-2σ,5-(disubstituted)-perhydro-*endo*-4,7-methanoindene.

[18] P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc.* (*A*), 1970, 363.

[19] D. R. Coulson, *J. Amer. Chem. Soc.*, 1969, **91**, 200.

p.p.m.), but the signals for the *ortho*-protons of the bipy ligand were well separated (0.27 p.p.m.).

Similar products were obtained on treating the complexes (III; alkenyl = $C_{10}H_{12}$, X = Cl, L = PPh_3) with sodium methoxide in the presence of one molar equivalent of PPh_3. The products are stable, white, sparingly soluble, solids; the dimethoxy-complex is monomeric in dichloromethane. Owing to the low solubility, n.m.r. spectra were of poor quality, but the complex $[Pt\{C_{10}H_{12}NHPh(OMe)\}(PPh_3)_2]$ showed a single sharp signal at τ 7.62 attributable to the CH_3O group. The high-field shift of *ca.* 1 p.p.m. relative to the corresponding bipyridyl complex is presumably due to the shielding effect of the phosphine in the *cis* position. Similar shielding of the protons of the anilino-group also occurred; the signal for the *ortho*-protons was shifted more than that of the *para*-proton and was also split, showing the non-equivalence of these protons. In the dimethoxy-complex two close CH_3O signals were found, with the same separation as those in the corresponding bipyridyl complex, again shifted to higher field (τ 7.62 and 7.65).

TABLE 7

N.m.r. data (τ) for alkylene complexes. Intensities are given in parentheses

	$Pt\{C_7H_8(OMe)_2\}(bipy)]$	$[Pt\{C_{10}H_{12}(OMe)_2\}(bipy)]$	$[Pt\{C_{10}H_{12}NHPh(OMe)\}(bipy)]$ [a]	$[Pt\{C_{10}H_{12}(OMe)_2\}(PPh_3)_2]$	$[Pt\{C_{10}H_{12}NHPh(OMe)\}(PPh_3)_2]$ [b]
H^6-bipy	0.84 (d) (2)	0.55 (d) (1), 0.82 (d) (1)	0.88 (d) (1), 0.94 (d) (1)		
$H^{3,4}$-bipy	1.97 (c) (4)	1.95 (c) (4)	2.10 (c) (4)		
H^5-bipy	2.51 (d) (2)	2.50 (c) (2)	2.56 (c) (2)		
MeOC*H*	6.35 (s) (2)	5.75 (d) (1), 5.95 (s) (1)	5.8 (c) (1)	*ca.* 6.5	*ca.* 6.6 [c]
PhNHC*H*			6.27 (d) (1)		7.34 (b) (1)
CH_3O	6.63 (s) (6)	6.63 (s), 6.66 (s) (6)	6.64 (s) (3)	7.62 (s), 7.65 (s)	7.62 (s) (3)
PtC*H*	8.14 (t) (1) [d]	8.09 (?)	7.84 (1) (?)		8.49 (1) (?)

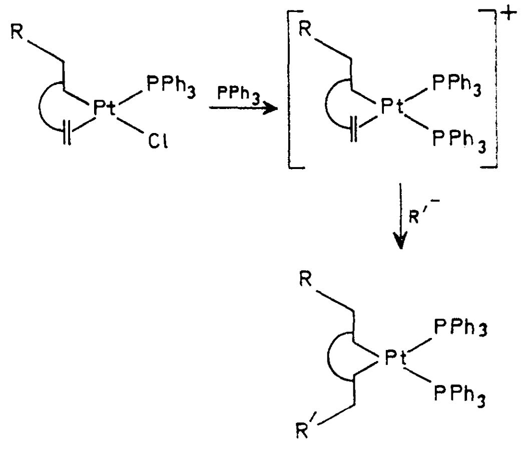
[a] *Ortho*- *meta*-, and *para*-protons of NHPh group: τ 3.37 (d) (2); 3.01 (t) (2); 3.51 (t) (1). [b] *Ortho*-, *meta*-, and *para*-protons of NHPh group; τ 3.97 (d) (1), 4.00 (d) (1); obscured by PPh_3 resonances; 3.53 (t) (1). [c] Obscured by OEt_2 resonance. [d] $^2J(PtCH)$ 126 Hz.

When (III; alkenyl = $C_{10}H_{12}$, R = NHPh, X = Cl, L = PPh_3) was treated with aniline, PPh_3, and a strong base (NEt_3 or $Na_2[CO_3]$), a slow reaction occurred to give an insoluble white product and $[NHEt_3]Cl$ or NaCl. Analysis of the residual liquor showed quantitative removal of chloride from the starting material. Analytical and i.r. data for the product indicated that it is a bis(triphenylphosphine) derivative, presumably formed by abstraction of hydrogen chloride from the original complex and addition of 1 mol of the phosphine, and we tentatively suggest formulation as the π-allylic derivative (XIII). The same material was obtained when the aniline was omitted. A similar product has been obtained from dichlorodicyclopentadienepalladium(II).[20]

DISCUSSION

The reactions described above demonstrate several features of the interactions of diene complexes with nucleophiles. First, there is a clear steric influence in the reactivity order $OMe^- > OPr^{n-} > OPr^{i-} > OBu^{t-}$. Steric interactions were demonstrated in the restricted rotation of isopropoxy-groups in some of our compounds. Secondly, with the sulphur-containing nucleophiles, used here for the first time, there is competition between the diene and the platinum. The more reactive diene,[2] dicyclopentadiene, undergoes nucleophilic attack whereas norbornadiene complexes react only by substitution at platinum.

The monosubstituted-alkenyl complexes (III; L = PPh_3) and (VII; L-L = bipy) react much more readily with methoxide ion than the precursor complexes (I). In the case of the bipyridyl complexes, the enhanced susceptibility to nucleophilic attack is presumably due to the positive charge on the complex. It seems likely that the phosphine complexes (III) react by a similar route, since reaction occurs only in the presence of excess of ligand, which presumably displaces chloride ion to give a cationic complex which then undergoes rapid nucleophilic attack. This mechanism is consistent with the two previous reports of similar reactions. When $[Pd(C_8H_{12}{\cdot}pd)(pd)]$ (pd = pentane-2,4-dionato-anion, C_8H_{12} = 8-substituted-cyclo-oct-5-enyl) is treated with two molar equivalents of PPh_3 the co-ordinated keto-enolate anion is displaced and attacks the olefin, giving $[Pt(C_8H_{12}{\cdot}2pd)(PPh_3)_2]$.[21] Similarly, the rapid addition of four molar equivalents of the phosphine to $[\{Pt\{C_7H_8(O_2CMe)\}(O_2CMe)\}_2]$ [$C_7H_8(O_2CMe)$ = 6-acetoxynorbornenyl] gives the diacetoxy-product $[Pt\{C_7H_8(O_2CMe)_2\}(PPh_3)_2]$.[7] In both cases the cation produced by phosphine substitution reacts with the displaced anion, acting as a nucleophile.



The latter example is of interest since the reaction of the related chloro-complexes, $[\{Pt(C_7H_8R)Cl\}_2]$, with tertiary phosphines leads to rearrangement to nortricyclenyl derivatives (VIII) and (IX). Here the displaced anion is a weak nucleophile and the rearrangement reaction takes precedence. With the stronger nucleophile $MeCO_2^-$ nucleophilic attack occurs much more rapidly than rearrangement. A slow rearrangement reaction was observed in the case of $[Pt(C_7H_8OMe)(dppe)]^+$, which may indicate that this reaction is slower

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[20] J. Tsuji and H. Takahashi, *J. Amer. Chem. Soc.*, 1968, **90**, 2387.

in cationic species than in neutral complexes of the type $[Pt(C_7H_8R)Cl(PR''_3)]$ which are the presumed intermediates in the reaction of the dimeric complexes.

The n.m.r. data for complexes (III) provide an interesting indication of the *trans* influence. *cis* Influences no doubt also operate, but these are much smaller and are complicated by shielding effects. In (III; alkenyl = $C_{10}H_{12}$) the chemical shifts and platinum-coupling constants of the vinylic protons decrease in the order L = Cl > py > PPh_3 for ligands, L, *trans* to the double bond, and similar trends are found for the acetato-[7] and thiocyanato-complexes. Decreases in coupling constants with increasing *trans* influence have been noted in several other systems and this appears to be a general phenomenon.[22] On the basis of the chemical shifts (and coupling constants where available) the following ligands may be rated in order of increasing *trans* influence: $MeCO_2^-$(br) ~ Cl^-(br) < SPh^-(br) < py < dppe < PPh_3 (br = bridging).

TABLE 8

Analytical data

Complex	M.p. (θ_c/°C)	Analysis (%)						*M*
		Found			Calc.			
		C	H	Other	C	H	Other	
$[\{Pt(C_7H_8OMe)Cl\}_2]$	118—120 (decomp.)	27.6	3.3		27.2	3.1		
$[\{Pt(C_7H_8OPr^i)Cl\}_2]$	102—104 (decomp.)	31.6	4.1		31.5	3.9		
$[\{Pt(C_{10}H_{12}OPr^i)Cl\}_2]$	194—196 (decomp.)	36.8	4.5		37.0	4.5		
$[Pt(C_{10}H_{12}NH_2Ph)Cl_2]$	194—198 (decomp.)	39.0	4.1	3.0 (N)	39.1	3.9	2.9 (N)	
$[\{Pt(C_{10}H_{12}NHPh)Cl\}_2]$	182—184 (decomp.)	41.4	4.0	3.1 (N)	41.5	4.0	3.1 (N)	
$[Pt(C_{10}H_{12}NHPh)Cl(NH_2Ph)]$	171—173 (decomp.)	48.8	4.9	5.3 (N)	48.5	4.7	5.1 (N)	
$[\{Pt(C_7H_8NHPh)Cl\}_2]$	89—93 (decomp.)	37.9	4.8	3.5 (N)	37.6	3.4	3.4 (N)	
$[Pt(C_7H_8)(SCN)_2]$	206—220 (decomp.)	27.0	2.4	6.6 (N)	26.8	2.0	6.9 (N)	
$[Pt(C_8H_{12})(SCN)_2]$	238—258 (decomp.)	28.6	3.1	6.9 (N)	28.6	2.9	6.7 (N)	
$[\{Pt(C_{10}H_{12}NCS)(SCN)\}_2]$	167—170 (decomp.)	32.9	3.1	5.9 (N)	32.5	2.7	6.3 (N)	
$[Pt(C_7H_8)Cl(SPh)]$	163—165 (decomp.)	35.4	2.7		36.2	3.0		
$[Pt(C_7H_8)(SPh)_2]$	179—184 (decomp.)	45.0	3.6		45.2	3.6		500 (505)
$[Pt(C_{10}H_{12})Cl(SPh)]$	160—165 (decomp.)	41.2	3.8	6.6 (S)	40.8	3.6	6.8 (S)	
$[\{Pt(C_{10}H_{12}SPh)(SPh)\}_2]$	180—185 (decomp.)	48.9	4.6	10.9 (S)	48.6	4.1	11.5 (S)	1 092 (1 090)
$[Pt(C_8H_{12})(SPh)_2]$	197—208 (decomp.)	45.4	4.2	12.5 (S)	46.0	4.2	12.3 (S)	
$[Pt(C_7H_8OMe)Cl(py)]$	96	36.2	3.8	2.9 (N)	36.1	3.7	2.9 (N)	
$[Pt(C_7H_8OPr^i)Cl(py)]$	100—102 (decomp.)	39.4	4.0	3.1 (N)	39.2	4.3	3.05 (N)	
$[Pt(C_7H_8NHPh)Cl(py)]$	92 (decomp.)	43.1	4.0	5.7 (N)	43.8	4.0	5.7 (N)	
$[Pt(C_{10}H_{12}OMe)Cl(py)]$	168—172 (decomp.)	40.7	4.3	3.2 (N)	40.7	4.25	3.0 (N)	
$[Pt(C_{10}H_{12}OPr^i)Cl(py)]$	156—160 (decomp.)	43.2	4.9	3.0 (N)	43.2	4.8	2.8 (N)	
$[Pt(C_{10}H_{12}NHPh)Cl(py)]\cdot0.5OEt_2$	129	48.5	5.0	5.0 (N)	48.4	4.8	4.9 (N)	
$[Pt(C_{10}H_{12}NCS)(py)(SCN)]$		40.2	4.0	7.8 (N) 12.7 (S)	39.3	3.0	8.1 (N) 12.3 (S)	
$[Pt(C_{10}H_{12}\cdot H_2NC_6H_4Me\text{-}p)(SCN)_2]$		41.8	3.9	7.8 (N)	41.5	3.7	7.6 (N)	
$[Pt(C_7H_8OMe)(bipy)]Cl$	148—154 (decomp.)	42.2	4.0	5.1 (N)	42.5	3.7	5.5 (N)	
$[Pt(C_{10}H_{12}OMe)(bipy)]Cl\cdot0.5CH_2Cl_2$	166—168 (decomp.)	44.5	4.4	5.4 (N)	44.4	4.2	4.9 (N)	
$[Pt(C_{10}H_{12}NHPh)(bipy)]Cl\cdot0.33CH_2Cl_2$	177—180 (decomp.)	49.7	4.5	6.6 (N)	49.6	4.2	6.6 (N)	
$[Pt(C_{10}H_{12}OMe)Cl(PPh_3)]$	186—188 (decomp.)	53.0	4.5		53.1	4.6		
$[Pt(C_{10}H_{12}OPr^i)Cl(PPh_3)]$	179—183 (decomp.)	54.5	5.3		54.5	5.0		
$[Pt(C_{10}H_{12}NHPh)Cl(PPh_3)]$	164—166 (decomp.)	56.8	4.8	1.9 (N)	57.0	4.6	1.9 (N)	
$[Pt(C_{10}H_{12}NCS)(PPh_3)(SCN)]$	150—152 (decomp.)	50.9	3.9	4.1 (N)	51.0	3.8	4.0 (N)	
$[\{Pt(C_7H_8OMe)Cl(PPh_3)\}_2]$	178—182 (decomp.)	50.7	4.2		50.5	4.2		1 310 (1 230)
$[\{Pt(C_7H_8OPr^i)Cl(PPh_3)\}_2]$	174—176 (decomp.)	52.3	4.7		52.2	4.7		1 280 (1 286)
$[\{Pt(C_7H_8NHPh)Cl(PPh_3)\}_2]$	149—153 (decomp.)	55.0	4.3	2.1 (N)	55.3	4.6	2.3 (N)	
$[Pt(C_7H_8OMe)Cl(PPh_3)_2]$	147—150 (decomp.)	60.2	4.7		60.0	4.8		864 (877)
$[Pt(C_7H_8OPr^i)Cl(PPh_3)_2]$	143—147 (decomp.)	61.0	5.0		60.1	5.0		887 (905)
$[\{Pt(PPh_3)(SPh)_2\}_2]$		54.7	4.2		54.2	3.8		
$[\{PtCl(PPh_3)(SPh)\}_2]$		48.1	3.6		48.0	3.3		
$[Pt(C_7H_8OMe)Cl(PEt_3)_2]$		40.9	6.9		40.8	7.0		
$[Pt(C_7H_8OMe)Cl(dppe)]$		54.5	4.8		54.4	4.8		
$[Pt\{C_{10}H_{12}(OMe)_2\}(PPh_3)_2]$	172—174 (decomp.)	62.8	5.2		63.1	5.2		908 (913)
$[Pt\{C_{10}H_{12}NHPh(OMe)\}(PPh_3)_2]$	174—176 (decomp.)	65.1	5.3	1.8 (N)	65.4	5.2	1.5 (N)	
$[Pt\{C_{10}H_{12}(OMe)_2\}(bipy)]$	204—207 (decomp.)	50.8	4.8	4.9 (N)	50.8	4.9	4.9 (N)	
$[Pt\{C_{10}H_{12}NHPh(OMe)\}(bipy)]$	214—217 (decomp.)	53.1	4.8	6.9 (N)	53.4	4.8	7.0 (N)	
$[Pt\{C_7H_8(OMe)_2\}(bipy)]$	154—156 (decomp.)	44.6	4.6	5.7 (N)	45.2	4.4	5.6 (N)	
$[Pt(C_{10}H_{11}OMe)(PPh_3)_2]$		63.1	5.0		63.9	5.1		

EXPERIMENTAL

Analytical data for new complexes are given in Table 8. N.m.r. ($CDCl_3$ solutions) and i.r. (solid mulls) spectra were

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[21] B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian, and D. White, *J. Chem. Soc.* (*A*), 1969, 1793.

[22] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

recorded on Varian HA 100 and Perkin-Elmer 621 spectrometers. The complexes $[Pt(diene)Cl_2]$ and $[\{Pt(C_{10}H_{12}OMe)Cl\}_2]$ were prepared by established methods.[2,23]

$[\{Pt(C_7H_8R)Cl\}_2]$ (R = OMe *or* OPr^i).—The literature method for the preparation of $[\{Pt(C_7H_8OMe)Cl\}_2]$ was found to give a high proportion of decomposition products. The following method is preferable. To $[Pt(C_7H_8)Cl_2]$ (0.45 g, 1.25 mmol), suspended in methanol (10 cm^3) at 55 °C, was added Na(OMe) (0.07 g, 1.25 mmol) in methanol (5 cm^3) over 5 min. The mixture was rapidly evaporated to dryness under reduced pressure, and extracted with dichloromethane. Hexane was added to the filtered extract, which was then concentrated in a stream of nitrogen, yielding white crystals of $[\{Pt(C_7H_8OMe)Cl\}_2]$ (0.32 g, 0.45 mmol, 72%).

The corresponding *isopropoxy-complex* was obtained in 62% yield similarly using $Na(OPr^i)$ at 60—65 °C with a reaction time of 30 min. Sodium t-butoxide at 70 °C gave rapid deposition to a brown tar.

$[\{Pt(C_{10}H_{12}OPr^i)Cl\}_2]$.—Sodium carbonate (*ca.* 0.2 g) was added to a suspension of $[Pt(C_{10}H_{12})Cl_2]$ (0.40 g, 1.00 mmol) in isopropyl alcohol (40 cm^3) and the mixture was stirred at 65 °C for 45 min. The insoluble product was extracted with dichloromethane and the extracts, after filtration, were reduced in volume at reduced pressure. Addition of diethyl ether afforded white crystals of the *product* (0.31 g, 0.37 mmol, 74%).

No reaction occurred in t-butyl alcohol at 65—70 °C during 90 min. After 120 min at 80 °C the i.r. spectrum of the crude product indicated trace amounts of $[\{Pt(C_{10}H_{12}OBu^t)Cl\}_2]$. Higher temperatures or longer reaction times gave only brown tars.

$[Pt(C_{10}H_{12}NH_2Ph)Cl_2]$, $[\{Pt(C_{10}H_{12}NHPh)Cl\}_2]$, *and* $[\{Pt(C_7H_8NHPh)Cl\}_2]$.—Aniline (0.10 g, 1.07 mmol) was added to a solution of $[Pt(C_{10}H_{12})Cl_2]$ (0.40 g, 1.00 mmol) in dichloromethane (25 cm^3) and the mixture stirred for 2 h and then allowed to stand at 0 °C for 12 h. The precipitated white *solid*, $[Pt(C_{10}H_{12}NH_2Ph)Cl_2]$, was filtered off and washed with water, ethanol, and diethyl ether (0.43 g, 0.88 mmol, 88%). This complex (0.40 g, 0.82 mmol) was suspended in dichloromethane, triethylamine (0.08 g, 0.80 mmol) was added, the mixture was stirred for 30 min, and then reduced to small bulk under reduced pressure. Diethyl ether was added until precipitation began and the mixture was kept at 0 °C for 12 h, after which the white *solid* was filtered off and washed several times with water, then with ethanol and diethyl ether, giving $[\{Pt(C_{10}H_{12}NHPh)Cl\}_2]$ (0.28 g, 0.31 mmol, 76%). The dehydrochlorination could also be effected with excess of sodium carbonate suspended in dichloromethane or acetone over 6 d. With aniline (2.05 mmol), in the presence of NEt_3 (1.00 mmol), *white* $[Pt(C_{10}H_{12}NHPh)Cl(NH_2Ph)]$ was obtained (59%).

The corresponding *norbornenyl derivative*, $[\{Pt(C_7H_8NHPh)Cl\}_2]$, was obtained similarly in 67% yield by adding NEt_3 dropwise over 20 min to a dichloromethane solution of $[Pt(C_7H_8)Cl_2]$ and aniline. Similar rapid reactions occurred with n-butylamine or diethylamine giving amorphous white products which could not be satisfactorily purified. The i.r. spectra indicated that nucleophilic attack by the amine had occurred.

$[Pt(C_7H_8)(SCN)_2]$ *and* $[Pt(C_8H_{12})(SCN)_2]$.—Potassium thiocyanate (0.22 g, 2.30 mmol) was stirred with a suspension of $[Pt(C_7H_8)Cl_2]$ (0.40 g, 1.10 mmol) for 30 min. The solvent was removed and the residue extracted with dichloromethane. The extract was filtered, concentrated, and diethyl ether was added, giving pale yellow *crystals* of $[Pt(C_7H_8)(SCN)_2]$ (0.33 g, 0.72 mmol, 67%). The corresponding yellow crystalline *cyclo-octa-*1,5*-diene complex* was obtained similarly in 79% yield.

$[\{Pt(C_{10}H_{12}NCS)(SCN)\}_2]$.—Potassium thiocyanate (0.19 g, 2.00 mmol) was added to a suspension of $[Pt(C_{10}H_{12})Cl_2]$ (0.40 g, 1.00 mmol) in acetone (25 cm^3) and the mixture was heated under reflux for a few minutes and then evaporated to dryness. The residue was washed with water, dissolved in dichloromethane, and reprecipitated by the addition of diethyl ether, giving pale yellow *crystals* (0.26 g, 0.25 mmol, 50%).

The Reactions of Benzenethiolate with $[Pt(diene)Cl_2]$.—Benzenethiol (0.12 g, 1.10 mmol) in acetone (5 cm^3) was added dropwise over 30 min to an acetone (25 cm^3) suspension of $[Pt(C_7H_8)Cl_2]$ (0.40 g, 1.10 mmol) and $Na_2[CO_3]$ (*ca.* 0.25 g). The solvent was removed and the solid residue extracted with dichloromethane. The extract was filtered, concentrated, and treated with diethyl ether, giving yellow *crystals* of $[Pt(C_7H_8)Cl(SPh)]$ (0.39 g, 0.90 mmol, 82%).

Similar reactions gave yellow *crystals* of $[Pt(C_{10}H_{12})Cl(SPh)]$ (77%) as a mixture of isomers. Use of double the quantity of benzenethiol gave yellow *crystals* of $[Pt(C_7H_8)(SPh)_2]$ (83%), $[Pt(C_8H_{12})(SPh)_2]$ (75%), and $[\{Pt(C_{10}H_{12}SPh)(SPh)\}_2]$ (81%).

Pyridine Adducts.—Reactions of chloro-bridged dimers were carried out in dichloromethane solution by stirring with two molar equivalents of pyridine for 30 min. The solution was then filtered, evaporated to small bulk, and treated with diethyl ether. The crystalline *products* separated when the mixture was kept at 0 °C for 12 h. The complexes $[Pt(alkenyl{\cdot}R)Cl(py)]$ (R = OMe, OPr^i, or NHPh; alkenyl = C_7H_8 or $C_{10}H_{12}$) were obtained in 74—91% yield; $[Pt(C_{10}H_{12}NHPh)Cl(py)]$ was obtained with 0.5 mol of diethyl ether of crystallisation.

To the complex $[\{Pt(C_{10}H_{12}NCS)(SCN)\}_2]$ (0.20 g, 0.23 mmol) in dichloromethane (50 cm^3) was added pyridine (0.04 g, 0.50 mmol). After stirring for 6 h the mixture was filtered and the solvent removed under reduced pressure. The tarry residue was shaken with diethyl ether for 12 h, giving a pink *solid*, $[Pt(C_{10}H_{12}NCS)(py)(SCN)]$ (0.15 g, 0.58 mmol, 63%), which retained some diethyl ether even after drying *in vacuo*.

The complex $[\{Pt(C_{10}H_{12}SPh)(SPh)\}_2]$ did not react with pyridine, but $[\{Pt(C_{10}H_{12}NCS)(SCN)\}_2]$ with *p*-toluidine after 14 h at room temperature gave a white *product* identified as $[Pt(C_{10}H_{12}{\cdot}H_2NC_6H_4Me\text{-}p)(SCN)_2]$ (85%).

2,2′-Bipyridyl Adducts.—The following general procedure was used. To the chloro-bridged dimer in dichloromethane solution was added 2,2′-bipyridyl (two molar equivalents) in dichloromethane, over 30 min. The resulting solution was filtered, concentrated to small bulk, and diethyl ether was added. White crystalline *products* were obtained in 80—90% yield, sometimes retaining some dichloromethane (confirmed by the n.m.r. spectra).

$[Pt(C_{10}H_{12}R)(PPh_3)X]$ (R = OMe, OPr^i, *or* NHPh, X = Cl; R = SCN, X = SCN).—To a solution of $[\{Pt(C_{10}H_{12}R)X\}_2]$ in dichloromethane was added two molar equivalents of triphenylphosphine and the mixture was shaken for 30 min, filtered, and concentrated to small bulk. Diethyl ether was added until a cloudiness appeared and the mixture was kept at 0 °C for 12 h, giving white *crystals*

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[23] R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Amer. Chem. Soc.*, 1960, **82**, 835.

which were washed with diethyl ether, yield 80—90%. The complex [{Pt($C_{10}H_{12}$SPh)(SPh)}$_2$] did not react, even after 16 h.

[{Pt(C_7H_8R)Cl(PPh_3)}$_2$] *and* [Pt(C_7H_8R)Cl(PPh_3)$_2$] (R = OMe, OPr^i, *or* NHPh).—A dichloromethane solution of [{Pt(C_7H_8R)Cl}$_2$] was shaken for 40 min with two molar equivalents of PPh_3, filtered, and reduced to small bulk. Diethyl ether (3 cm^3) and hexane were added until the solution became cloudy, after which it was kept at 0 °C for 16 h with occasional addition of further hexane to aid precipitation. White *solids* were formed, which were filtered off and washed with hexane (R = OMe or OPr^i, 85—87%). For R = NHPh, a reaction time of 3 h was required (yield 51%).

The above products [{Pt(C_7H_8R)Cl(PPh_3)}$_2$] (R = OMe or OPr^i) were treated in the same way with two further molar equivalents of PPh_3 yielding white *crystals* of [Pt(C_7H_8R)Cl(PPh_3)$_2$] (78—88%).

[Pt(PPh_3)XY] (X = Y = NCS *or* SPh; X = Cl, Y = SPh).—Triphenylphosphine (0.40 g, 1.0 mmol) was added to a dichloromethane solution of [Pt(C_7H_8)(SCN)$_2$] (0.40 g, 1.0 mmol) and the mixture was shaken for 70 min. After filtration, and evaporation to small bulk, diethyl ether was added and the mixture was kept at 0 °C for 12 h, giving the *complex* [{Pt(PPh_3)(SCN)$_2$}$_2$] (0.33 g, 0.29 mmol, 58%). The *complexes* [{Pt(PPh_3)(SPh)$_2$}$_2$] (88%) and [{PtCl(PPh_3)(SPh)}$_2$] (77%) were obtained similarly from [Pt(C_7H_8)(SPh)$_2$], [Pt(C_7H_8)Cl(SPh)], and [Pt($C_{10}H_{12}$)Cl(SPh)].

[Pt(C_7H_8OMe)Cl(PEt_3)$_2$].—Triethylphosphine (0.30 g, 2.5 mmol) was stirred with a dichloromethane solution of [{Pt(C_7H_8OMe)Cl}$_2$] (0.40 g, 0.57 mmol) for 60 min. Hexane (40 cm^3) was added to the filtered mixture, which was then evaporated slowly in a stream of nitrogen until cloudy, and allowed to stand at 0 °C for 12 h. The resulting solution was decanted from a tarry deposit, treated with hexane (60 cm^3), and evaporated to small bulk. On standing for 60 h at 0 °C, colourless *crystals* of [Pt(C_7H_8OMe)Cl(PEt_3)$_2$] were obtained (0.35 g, 0.59 mmol, 52%).

[Pt(C_7H_8OMe)(dppe)]Cl *and* [Pt(C_7H_8OMe)Cl(dppe)].—1,2-Bis(diphenylphosphino)ethane (0.45 g, 1.13 mmol) was added to a dichloromethane solution (10 cm^3) of [{Pt(C_7H_8OMe)Cl}$_2$] and the mixture shaken for 5 min. Excess of hexane was then added and the white *precipitate* filtered off and dried *in vacuo*. This product (0.55 g) was shown by n.m.r. to consist primarily of the ionic complex [Pt(C_7H_8OMe)(dppe)]Cl, containing *ca.* 20% of the nortricyclenyl complex, [Pt(C_7H_8OMe)Cl(dppe)]. A dichloromethane solution of the product (0.3 g) and dppe (*ca.* 0.01 g) was shaken for a further 14 h, filtered, and hexane was added. Evaporation under nitrogen gave a white solid (0.27 g), identified as [Pt(C_7H_8OMe)Cl(dppe)].

Reactions of 2,2′-*Bipyridyl Complexes with Methoxide Ion.*—The complex [Pt($C_{10}H_{12}$OMe)(bipy)]Cl (0.40 g, 0.73 mmol) in methanol (25 cm^3) was treated dropwise with sodium methoxide (0.04 g, 0.74 mmol) in methanol (10 cm^3) over 20 min at room temperature. The resulting solution was evaporated to dryness *in vacuo* and the residue extracted with benzene (70 cm^3). The filtered extract was concentrated to small bulk at 30 °C, excess of hexane was added, and the mixture was allowed to stand at 0 °C for 12 h, when *crimson crystals* of [Pt{$C_{10}H_{12}$(OMe)$_2$}(bipy)] were formed (0.23 g, 0.42 mmol, 58%). These were washed with water, diethyl ether, and hexane. The complex appeared to contain 0.4 mol of benzene, the presence of which was confirmed by the n.m.r. spectrum.

The *complexes* [Pt{$C_{10}H_{12}$NHPh(OMe)}(bipy)] (crimson, 77% yield) and [Pt{C_7H_8(OMe)$_2$}(bipy)] (orange, 78%) were obtained similarly except that they could be crystallised directly from the methanol solution.

Reactions of Triphenylphosphine Complexes with Methoxide Ion.—The complex [Pt($C_{10}H_{12}$OMe)Cl(PPh_3)] (0.40 g, 0.6 mmol) and PPh_3 (0.16 g, 0.61 mmol) suspended in methanol (20 cm^3) were treated dropwise over 30 min at room temperature with a solution of Na(OMe) (0.035 g, 0.65 mmol). The resulting solution was concentrated in a stream of nitrogen and cooled to 0 °C for 2 h. The solid thus obtained was washed with water to remove sodium chloride, then with ethanol and diethyl ether, and recrystallised from dichloromethane–diethyl ether giving the white *complex* [Pt{$C_{10}H_{12}$(OMe)$_2$}(PPh_3)$_2$] (0.43 g, 0.47 mmol, 77%).

The corresponding *anilino-complex*, [Pt{$C_{10}H_{12}$NHPh(OMe)}(PPh_3)$_2$] was obtained similarly (75%) from [Pt($C_{10}H_{12}$NHPh)Cl(PPh_3)].

Reaction of [Pt($C_{10}H_{12}$OMe)Cl(PPh_3)] *with Bases.*—The complex (0.40 g, 0.61 mmol) and PPh_3 (0.16 g, 0.61 mmol) in dichloromethane were treated with aniline (0.058 g, 0.62 mmol) and an equimolar quantity of base (sodium carbonate or triethylamine), and the mixture was shaken at room temperature for 6 d giving a white, sparingly soluble, *complex* and a water-soluble chloride (0.60 mmol). The same product was obtained in the absence of aniline.

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