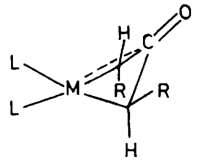
Chemistry of Metallacyclobutanones (η^3-Oxodimethylenemethane Complexes). Part 5.[1] Ligand Substitution Reactions of Metallacyclobutan-3-ones of Platinum(II) and Palladium(II) with Tertiary Phosphines and t-Butyl Isocyanide; Crystal Structures of $[\overline{\mathrm{Pt\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(CNBu^t)(AsPh_3)}]$ and $[\overline{\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C}}\mathrm{(\overset{+}{N}HBu^t)\}(CNBu^t)_2}]$ *

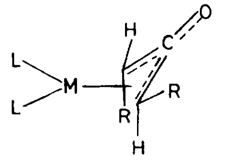
Raymond D. W. Kemmitt, Peter McKenna, David R. Russell, and Lesley J. S. Prouse
Department of Chemistry, The University, Leicester LE1 7RH

The ligands L displace triphenylarsine from the complexes $[\overline{\mathrm{M\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(AsPh_3)_2}]$ to give good yields of the complexes $[\overline{\mathrm{M\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}L_2}]$ (M = Pt, L = PPh_3, $PMePh_2$, PMe_2Ph, L_2 = $Ph_2PCH_2CH_2PPh_2$(dppe); M = Pd, L = PPh_3, L_2 = 2,2′-bipyridine). Treatment of the complexes $[\overline{\mathrm{M\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}L_2}]$ with one mole equivalent of t-butyl isocyanide gives the monosubstituted complexes $[\overline{\mathrm{M\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(CNBu^t)L}]$ (M = Pt or Pd, L = $AsPh_3$ or PPh_3). The single-crystal *X*-ray structure of $[\overline{\mathrm{Pt\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(CNBu^t)(AsPh_3)}]$ establishes the presence of a puckered platinacyclobutan-3-one ring [fold angle = 42(1)°] with the triphenylarsine ligand *trans* to the axial methoxycarbonyl group. The reactions of 1 mole equivalent of t-butyl isocyanide with $[\overline{\mathrm{Pt\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(CNBu^t)(PPh_3)}]$ or 2 mole equivalents of $CNBu^t$ with $[\overline{\mathrm{Pt\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(PPh_3)_2}]$ give the ring-expanded zwitterionic complex $[\overline{\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C}}\mathrm{{=}\overset{+}{N}HBu^t\}(CNBu^t)(PPh_3)}]$. Similar complexes $[\overline{\mathrm{Pt\{CH(COR)CO\overset{-}{C}(COR)C}}\mathrm{{=}\overset{+}{N}HBu^t\}(CNBu^t)_2}]$ are formed upon treatment of $[\overline{\mathrm{Pt\{CH(COR)COCH}}\mathrm{(COR)L_2}]$ (R = OMe, L = $AsPh_3$ or PPh_3; R = Me, L = PPh_3) with three mole equivalents of $CNBu^t$. The structure of $[\overline{\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C}}\mathrm{{=}\overset{+}{N}HBu^t\}(CNBu^t)_2}]$ was established by a single-crystal *X*-ray diffraction study.

We have recently developed synthetic routes to a novel series of metallacycles $[\overline{\mathrm{M(CHRCOCHR}}\mathrm{)L_2}]$ (M = Pd or Pt; R = ester, acyl, or phenyl substituent; L = tertiary-phosphine or -arsine) which can be formulated either as the metallacyclobutan-3-one species (**1a**) with transannular M ··· CO interactions or as the η^3-oxodimethylenemethane species (**1b**).[1-4] The availability of these systems afforded us the opportunity to investigate the chemistry of these complexes and compare their reactions with related metallacyclobutane complexes.[5,6] In this paper we report some ligand-substitution reactions of the complexes (**1**) and establish that reactions with t-butyl isocyanide lead to insertion and ring expansion of the metallacyclic ring. Some reactions with halogens and methyl iodide are also reported.



(**1a**)



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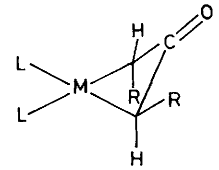

R = CO_2Me

	L or L_2	M
(**2a**)	$AsPh_3$	Pt
(**2b**)	PPh_3	Pt
(**2c**)	$PMePh_2$	Pt
(**2d**)	PMe_2Ph	Pt
(**2e**)	dppe	Pt
(**2f**)	$AsPh_3$	Pd
(**2g**)	PPh_3	Pd
(**2h**)	bipy	Pd

Results and Discussion

Preliminary studies using the platinum and palladium complexes $[\overline{\mathrm{M\{CH(CO_2Me)COCH}}\mathrm{(CO_2Me)\}(AsPh_3)_2}]$, (M = Pt or Pd) (**2a**) and (**2f**) established the facile displacement of triphenylarsine by other ligands. Thus treatment of (**2a**) with PPh_3, $PMePh_2$, PMe_2Ph, and $Ph_2PCH_2CH_2PPh_2$ gave the tertiary phosphine complexes (**2b**)—(**2e**) respectively and

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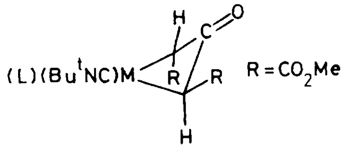
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: lbf in^{-2} ≈ 6 895 Pa.



	L	M
(3a)	$AsPh_3$	Pt
(3b)	PPh_3	Pt
(3c)	$AsPh_3$	Pd
(3d)	PPh_3	Pd

reaction of the palladium complex (**2f**) with PPh_3 afforded a quantitative yield of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$ (**2g**). Similar substitution reactions have been observed using the tetrafluoroethylene complex $[Pt(C_2F_4)(AsPh_3)_2]$.[7,8] However, although in these studies[7] we observed that 2,2′-bipyridine(bipy) displaced $AsPh_3$ from $[Pt(C_2F_4)(AsPh_3)_2]$, we have found that there is no reaction between (**2a**) and 2,2′-bipyridine under similar conditions. Treatment of the palladium complex (**2f**) with 2,2′-bipyridine does, however, lead to displacement of $AsPh_3$ to give $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(bipy)]$ (**2h**).

Some interesting substitution reactions also occur upon treatment of metallacyclobutan-3-one complexes with t-butyl isocyanide, the nature of the complex formed being very dependent upon the mole ratio of isocyanide used in the reaction. Thus the action of an equimolar proportion of t-butyl isocyanide upon the complexes (**2a**), (**2b**), (**2f**), and (**2g**) gave, in high yield, a series of air-stable monosubstituted complexes $[M\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)L]$ [M = Pt, L = $AsPh_3$ (**3a**), L = PPh_3 (**3b**); M = Pd, L = $AsPh_3$ (**3c**), L = PPh_3 (**3d**)]. Treatment of the triphenylarsine complexes (**3a**) and (**3c**) with triphenylphosphine in dichloromethane at room temperature resulted in displacement of co-ordinated $AsPh_3$ and formation of the triphenylphosphine derivatives (**3b**) and (**3d**) respectively. However, under forcing conditions, treatment of $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)]$ with excess of triphenylphosphine in refluxing dichloromethane resulted in displacement of both $CNBu^t$ and $AsPh_3$ ligands to afford the bis(triphenylphosphine) complex (**2b**).

The i.r. spectra of these t-butyl isocyanide complexes (Table 1) all exhibit a strong band around 2 200 cm^{-1} due to ν(CN) and the three maxima observed in the range 1 725—1 675 cm^{-1} are assigned to ν(CO) of the ester carbonyls. As observed for the parent complexes (**2**),[2,3] the palladium–ester carbonyl bands appear at slightly lower frequency. The oxodimethylenemethane carbonyl appears as a very strong band at around 1 650 cm^{-1} for the platinum complexes and 1 620 cm^{-1} for the palladium complexes. Again this follows the same trend observed in the parent complexes.[2,3] However, these observed frequencies for the ring carbonyls are much higher than those found for the parent complexes which occur in the range 1 615—1 635 cm^{-1} for the platinum complexes and 1 590—1 607 cm^{-1} for the palladium complexes.[2,3] These data suggest that the t-butyl isocyanide complexes (**3**) are less puckered and may have weaker transannular metal–carbon interactions.

A single-crystal *X*-ray diffraction study established the molecular structure of $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)]$ (**3a**), which is illustrated in Figure 1 with the crystallographic numbering. Relevant bond lengths and angles are given in Table 2. The molecule contains the *trans* disubstituted fragment $(MeO_2C)CHC(O)CH(CO_2Me)$ bonded to the $Pt(CNBu^t)(AsPh_3)$ moiety, with the triphenylarsine *trans* to the axial methoxycarbonyl. The co-ordination around platinum is square planar, with an almost zero twist angle of 0.4(4)° between the C(11)–Pt–As and C(1)–Pt–C(3) planes. Overall the geometry of (**3a**) is similar to the parent complexes $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}L_2]$ (**2**),[2] although there are notable differences. Thus, the Pt–C(1) and Pt–C(3) distances are shorter than those observed in $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$ (**2b**) and are closer in value to those found for the platinacyclobutane $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$,[9] the average Pt–C distances being 2.09 for (**3a**), 2.08 for $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$, and 2.15 Å for (**2b**). The fold angle between planes C(1)–Pt–C(3) and C(1)–C(2)–C(3) of 42(1)° is smaller than that found for (**2b**) [fold angle = 50.4(4)°],[2] although (**3a**) is more puckered than saturated platinacyclobutanes where the range[5] is from 0—30° {22.4° in $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$}.[9] The transannular Pt–C(2) distance for (**3a**) is lengthened by 0.1 Å compared with (**2b**). These changes in the bonding of the oxodimethylenemethane fragment to the metal are also manifested in the bond lengths of the fragment itself. Thus the C(2)–O(1) distance is shorter for (**3a**) at 1.21 Å compared with 1.23 Å for (**2b**), although in both compounds the C(2)–O(1) bond is inclined out of the C(1)–C(2)–C(3) plane towards the platinum [13(1) in (**3a**) and 11.6(5)° in (**2b**)]. Furthermore, the average of the C(1)–C(2) and C(2)–C(3) bond lengths is longer for (**3a**) (1.50 Å) than for (**2b**) (1.48 Å). We therefore conclude that (**3a**) has less oxodimethylenemethane character compared with the parent complexes (**2**), and exhibits more similarity to platinacyclobutane complexes. The *X*-ray data thus support the interpretation placed on the i.r. spectral data, and the general structural changes found for (**3a**) compared with the complexes (**2**) can be assumed for the other monosubstituted t-butyl isocyanide complexes, (**3**).

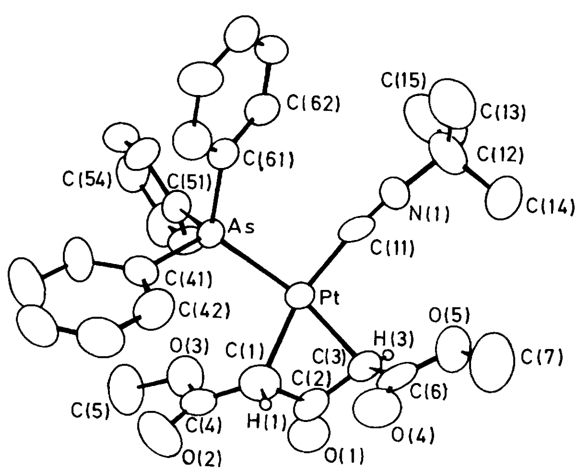


Figure 1. Molecular structure of the complex $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)]$ (**3a**) with hydrogens omitted, except those of the metallacyclic ring

The ^1H n.m.r. spectra of the complexes (**3**), measured at room temperature, exhibited the expected features for either a static or rapidly inverting ring, the ester methyl groups and CH ring protons always being inequivalent due to the complex having mixed donor ligands. Furthermore, there were no significant changes observable in the ^1H n.m.r. data at either low or high temperature (−95 to +90 °C). These data suggest three possibilities; that a lower temperature is required to observe the two static structures, that the complex is rigid, or that the

Table 1. I.r. spectra (2 250—1 600 cm^{-1}) of the metallacyclobutan-3-one complexes $[\mathrm{M\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(L)}]$*

M	L	ν(CN)/cm^{-1}	ν(CO)$_{\mathrm{ester}}$/cm^{-1}	ν(CO)$_{\mathrm{ring}}$/cm^{-1}
Pt	AsPh$_3$	2 188vs	1 725s, 1 709s, 1 687vs	1 652vs
Pt	PPh$_3$	2 186vs	1 718s, 1 702s, 1 680vs	1 646vs
Pd	AsPh$_3$	2 208vs	1 721s (sh), 1 700vs, 1 677vs	1 623vs
Pd	PPh$_3$	2 208vs	1 720s, 1 700vs, 1 675vs	1 620vs

* Recorded as KBr discs.

Table 2. Selected bond lengths (Å) and bond angles (°) in $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)}]$ (**3a**)

				CNBu^t ligand			
Pt–As	2.398(1)	Pt–C(1)	2.057(14)	C(11)–N(1)	1.143(14)	N(1)–C(12)	1.471(16)
Pt–C(11)	1.933(11)	Pt–C(2)	2.509(13)				
		Pt–C(3)	2.121(10)				
CH(CO$_2$Me)COCH(CO$_2$Me) ligand				AsPh$_3$ ligand			
C(1)–C(2)	1.509(17)	O(3)–C(5)	1.494(19)	As–C(41)	1.919(7)	As–C(51)	1.935(7)
C(2)–C(3)	1.492(17)	C(3)–C(6)	1.473(18)	As–C(61)	1.934(6)		
C(2)–O(1)	1.215(15)	C(3)–H(3)	0.94(7)				
C(1)–H(1)	0.96(8)	C(6)–O(4)	1.191(16)				
C(1)–C(4)	1.501(21)	C(6)–O(5)	1.345(17)				
C(4)–O(2)	1.206(17)	O(5)–C(7)	1.470(21)				
C(4)–O(3)	1.327(18)						
				CNBu^t ligand			
C(11)–Pt–As	95.7(3)	C(11)–Pt–C(3)	95.9(4)	Pt–C(11)–N(1)	173.1(9)	N(1)–C(12)–C(13)	107.8(10)
As–Pt–C(1)	100.3(4)	C(1)–Pt–C(3)	68.1(5)	C(11)–N(1)–C(12)	174.6(10)	N(1)–C(12)–C(14)	103.3(11)
						N(1)–C(12)–C(15)	107.7(13)
CH(CO$_2$Me)COCH(CO$_2$Me) ligand							
C(1)–C(2)–C(3)	102.6(10)	H(1)–C(1)–C(4)	107(5)	C(4)–O(3)–C(5)	118.2(11)	C(2)–C(3)–H(3)	112(5)
C(1)–C(2)–O(1)	130.0(12)	H(1)–C(1)–C(2)	104(4)	Pt–C(3)–C(2)	86.1(6)	C(3)–C(6)–O(5)	112.1(11)
C(3)–C(2)–O(1)	125.1(10)	C(4)–C(1)–C(2)	113.4(11)	Pt–C(3)–H(3)	109(5)	C(3)–C(6)–O(4)	124.6(12)
Pt–C(1)–C(2)	88.0(8)	C(1)–C(4)–O(2)	126.1(14)	Pt–C(3)–C(6)	105.9(7)	O(4)–C(6)–O(5)	123.3(12)
Pt–C(1)–H(1)	115(5)	C(1)–C(4)–O(3)	113.4(11)	H(3)–C(3)–C(6)	118(5)	C(6)–O(5)–C(7)	114.3(11)
Pt–C(1)–C(4)	126.2(11)	O(2)–C(4)–O(3)	120.4(13)	C(2)–C(3)–C(6)	120.1(11)		
AsPh$_3$ ligand				Torsion angles			
Pt–As–C(41)	115.7(2)	C(41)–As–C(61)	102.2(3)	C(11)–Pt–C(3)–H(3)	−43(5)	As–Pt–C(1)–H(1)	−100(4)
Pt–As–C(51)	113.3(2)	C(41)–As–C(51)	105.3(3)				
Pt–As–C(61)	116.6(2)	C(51)–As–C(61)	102.2(3)				

Table 3. ^{1}H N.m.r. data for the metallacyclobutan-3-one complexes $[\mathrm{M\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)L}]$*

Chemical shifts and coupling constants	Complex			
	(**3a**)	(**3b**)	(**3c**)	(**3d**)
δ(H)	4.44	4.46	4.64	4.62
^2J(PtH)	88.7	71.8		
^3J(PH)		11.5		11.4
δ(H)	3.90	3.69	4.02	3.79
^2J(PtH)	49.3	46.0		
^3J(PH)		4.8		6.0
δ(Me)$_{\mathrm{ester}}$	3.67	3.70	3.70	3.69
δ(Me)$_{\mathrm{ester}}$	2.94	3.00	2.93	2.97
δ(Me)$_{\mathrm{t\text{-}butyl}}$	1.15	1.16	1.23	1.20

* Chemical shifts in p.p.m. relative to SiMe$_4$, coupling constants in Hz.

equilibrium between the two conformers lies far to one side so that the concentration of one conformer is too small to be observed. It is not possible to distinguish between these possibilities from the ^{1}H n.m.r. data. The complexes (**3b**)—(**3d**) behave similarly and some of the important chemical shifts and coupling constants for the complexes (**3**) are listed in Table 3.

The observed geometry of the triphenylarsine complex (**3a**) allows assignment of the ^{1}H n.m.r. spectrum, assuming a static structure in solution, with the signal at δ 4.44 showing a large ^{195}Pt coupling, ^2J(PtH) 88.7 Hz, assigned to the axial hydrogen H(1) which is *trans* to t-butyl isocyanide, and the signal at 3.90 p.p.m. with a smaller ^{195}Pt coupling, ^2J(PtH) 49.3 Hz, assigned to the equatorial hydrogen H(3) which is *trans* to the triphenylarsine. These assignments are based on previous observations that the ^{195}Pt coupling to axial hydrogens is greater than that to equatorial hydrogens.[2,4] The angles between the vector on platinum perpendicular to the C(1)–Pt–C(3) plane and the C(1)–H(1) and C(3)–H(3) vectors are 27(5) and 50(5)° respectively, and the distances from platinum to H(1) and H(3) are 2.61(8) an 2.59(7) Å respectively for (**3a**).

Although in the triphenylarsine complex (**3a**) the axial hydrogen H(1) is *trans* to t-butyl isocyanide, examination of the n.m.r. data for the t-butyl isocyanide–platinum and –palladium complexes (**3b**) and (**3d**) (Table 3) indicates that in both the axial hydrogen is *trans* to the triphenylphosphine ligand. Thus the high-frequency resonances, assignable to the axial hydrogens, at 4.46 and 4.62 p.p.m. in (**3b**) and (**3d**) respectively, have large

Table 4. ^{13}C-{^{1}H} N.m.r. data for the oxodimethylenemethane fragment of the complexes [$\overline{\text{M}\{\text{CH(CO}_2\text{Me)COC}}\text{H(CO}_2\text{Me)}\}(\text{CNBu}^t)\text{L}$] *

Chemical shifts and coupling constants	Complex (**3a**)	(**3b**)	(**3d**)
δ $C^{\beta}_{\text{ring carbonyl}}$	179.8	179.6	175.2
^2J(PtC)	189.4	177	
^3J(PC)		5.8	5.6
δ $\text{C(CO)}_{\text{eq. ester}}$	173.1	173.5	172.9
^2J(PtC)	31.3	25.8	
δ $\text{C(CO)}_{\text{axial ester}}$	171.7	171.7	170.5
^2J(PtC)	52.6	55.0	
δ Me	50.7	50.7	50.7
δ Me	49.9	50.2	50.1
δ $C^{\alpha}_{trans\ \text{to Bu}^t\text{NC}}$	48.8	51.3	56.9
^1J(PtC)	288.8	293	
^2J(PC)		2	0
δ $C^{\alpha}_{cis\ \text{to Bu}^t\text{NC}}$	48.2	51.0	55.7
^1J(PtC)	267.7	216.5	
^2J(PC)		54.1	49.2

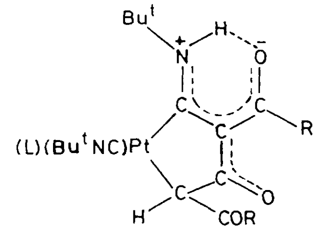
* Chemical shifts in p.p.m. relative to $SiMe_4$, coupling constants in Hz.

Table 5. Selected bond lengths (Å) and bond angles (°) for [$\overline{\text{Pt}\{\text{CH(CO}_2\text{Me)CO}\bar{\text{C}}\text{(CO}_2\text{Me)C}}=\overset{+}{\text{N}}\text{HBu}^t\}(\text{CNBu}^t)_2$] (**4a**)

Pt–C(1)	1.983(7)	C(1)–N(1)	1.144(9)
Pt–C(2)	1.993(8)	N(1)–C(11)	1.475(10)
Pt–C(3)	2.098(6)	C(2)–N(2)	1.154(9)
Pt–C(4)	2.064(6)	N(2)–C(21)	1.470(8)
C(41)–N(41)	1.467(7)	C(5)–C(6)	1.445(7)
N(41)–H(4)	0.95(8)	C(6)–O(6)	1.232(7)
N(41)–C(4)	1.327(6)	C(3)–C(6)	1.529(9)
C(4)–C(5)	1.424(7)	C(3)–H(3)	0.93(5)
C(5)–C(51)	1.440(8)	C(3)–C(31)	1.476(10)
C(51)–O(51)	1.219(7)	C(31)–O(31)	1.212(9)
C(51)–O(52)	1.337(7)	C(31)–O(32)	1.360(9)
C(52)–O(52)	1.455(12)	C(32)–O(32)	1.429(13)
C(1)–Pt–C(2)	93.1(3)	Pt–C(1)–N(1)	172.7(6)
C(2)–Pt–C(3)	86.9(3)	Pt–C(2)–N(2)	166.9(8)
C(3)–Pt–C(4)	80.0(2)	C(1)–N(1)–C(11)	177.0(7)
C(1)–Pt–C(4)	100.0(2)	C(2)–N(2)–C(21)	171.0(7)
Pt–C(3)–C(6)	102.5(4)	O(51)–C(51)–O(52)	119.2(6)
Pt–C(4)–C(5)	118.9(3)	C(5)–C(51)–O(52)	115.0(5)
Pt–C(4)–N(41)	130.8(4)	C(6)–C(5)–C(51)	123.3(5)
C(4)–N(41)–C(41)	132.8(6)	C(4)–C(5)–C(51)	122.3(4)
C(41)–N(41)–H(4)	98(3)	C(4)–C(5)–C(6)	113.6(5)
C(4)–N(41)–H(4)	129(3)	C(5)–C(6)–O(6)	126.9(6)
C(5)–C(4)–N(41)	118.1(5)	C(3)–C(6)–C(5)	114.7(4)
C(5)–C(51)–O(51)	125.3(5)	C(3)–C(6)–O(6)	118.4(4)

^3J(PH) couplings, around 11 Hz, and for the platinum complex (**3b**) a large ^2J(PtH) coupling of 71.8 Hz. The low frequency signals, assignable to the equatorial hydrogens have small ^3J(PH) couplings (Table 3) as observed in other metallacyclobutan-3-one complexes.[1-3] The energy difference between the conformation of the triphenylarsine complex and that of the triphenylphosphine complexes is presumably small and may depend mainly on the steric interactions of donor ligands with the oxodimethylenemethane fragment.

The ^{13}C-{^{1}H} n.m.r. spectra of the t-butyl isocyanide complexes (**3a**), (**3b**), and (**3d**) exhibited the expected resonances for the ring carbons (Table 4) and are assigned assuming rigid structures. As found for the complexes (**2**),[2] the β-carbons of the ring have large ^2J(PtC) and/or ^3J(PC) couplings compared with



	L	R
(**4a**)	Bu^{t}NC	OMe
(**4b**)	Bu^{t}NC	Me
(**4c**)	PPh$_3$	OMe

the β-carbons of the ester carbonyls. It is noticeable that one of the ester carbonyls has a larger ^2J(PtC) coupling than the other and this resonance is assigned to the axial ester carbonyl, since, like the axial hydrogen H(1) in (**3a**), the axial ester carbon C(6) may be expected to exhibit a greater coupling to the ^{195}Pt nucleus than the equatorial ester carbon C(4) [the distances between platinum and C(4) and C(6) are 3.18(1) and 2.90(1) Å respectively in (**3a**)]. For the two triphenylphosphine complexes (**3b**) and (**3d**) the assignment of the carbons bound to the metal is based on the magnitude of ^2J(PC) which would be expected to be larger for α-carbons *trans* to the phosphorus ligand than for α-carbons *cis* to phosphorus. The isocyanide carbon signals are not observed due either to overlapping with the phenyl resonances, or to the long relaxation time and low nuclear Overhauser effect associated with these carbons as observed, for example, in the complexes [$Pt_3(CNR)_6$].[10]

Reaction of (**2a**) with 3 mole equivalents of t-butyl isocyanide in refluxing dichloromethane resulted in complete displacement of triphenylarsine and incorporation of all three t-butyl isocyanides to form a new complex (**4a**). The complex (**4a**) was also formed upon treatment of (**2b**) with 3 mole equivalents of t-butyl isocyanide, and an analogous complex (**4b**) was formed by the reaction of t-butyl isocyanide with [$\overline{\text{Pt}\{\text{CH(COMe)COC}}\text{H(COMe)}\}(\text{AsPh}_3)_2$]. The microanalytical and spectroscopic data were insufficient to assign a molecular structure to the complexes (**4a**) and (**4b**) and a single-crystal *X*-ray structure determination was carried out on (**4a**).

The molecular structure of (**4a**) is illustrated in Figure 2 with the crystallographic numbering system. The complex consists of a five-membered metallacyclic ring attached to the Pt(CNBu^t)$_2$ moiety, and crystallises with one molecule of chloroform per molecule of complex incorporated in a 'hole' in the lattice. Important bond lengths and angles are given in Table 5. The co-ordination around the platinum atom is essentially square planar, with the twist between the C(1)–Pt–C(2) and C(4)–Pt–C(3) planes being 8.9(3)°. Examination of C(5) shows this carbon to be sp^2 hybridised, lying in the plane generated by C(4), C(51), and C(6) (Table 6). Thus C(5) can be considered as a planar (flat) carbanion stabilised by the two electron-withdrawing carbonyls attached to it. The C(5)–C(4), C(5)–C(51), and C(5)–C(6) bond lengths of 1.424(7), 1.440(8), and 1.445(7) Å respectively are short compared with carbon–carbon single bonds [C(3)–C(6) is 1.529(9) Å], suggesting a significant delocalisation of electron density. The positive charge localised on the nitrogen N(41) generates a zwitterionic complex with the N(41)–C(4) bond distance of 1.327(6) Å being typical of a carbon–nitrogen double bond. The hydrogen, H(4), is orientated towards the oxygen O(51), the O(51)–H(4) internuclear distance of 2.04(6) Å being indicative of a weak hydrogen bond. This, together with the electron-donating inductive effect of the tertiary butyl group, helps stabilise the

Table 6. Equations of some least-squares planes in the form $Ax + By + Cz = D$, for the complex (**4a**), where x, y, and z are fractional co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): C(4), C(6), C(51)
$10.947x - 6.8y - 1.1485z = 2.3195$
[C(5) −0.076]

Plane (2): H(4), N(41), C(4), C(5), C(6), O(6), C(51), O(51)
$10.6624x - 7.575y - 1.307z = 2.2766$
[H(4) 0.018, N(41) 0.034, C(4) −0.083, C(5) −0.041, C(6) 0.124, O(6) −0.069, C(51) 0.059, O(51) −0.042]

Plane (3): Pt, C(4), C(5), C(6), C(3)
$-11.1913x + 5.0737y + 0.3191z = -2.4046$
[Pt 0.245, C(4) −0.235, C(5) 0.068, C(6) 0.224, C(3) −0.302]

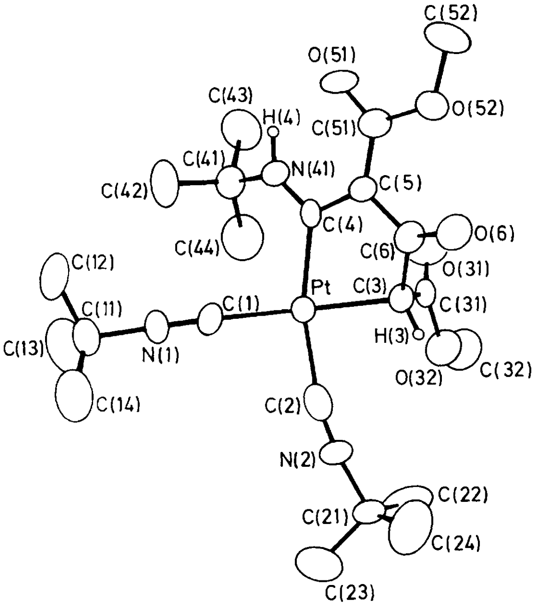
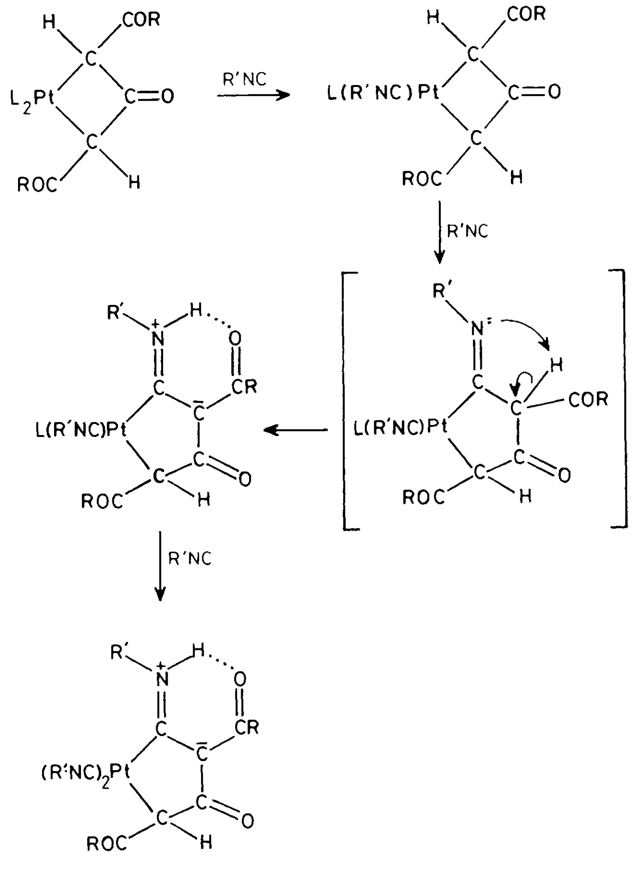


Figure 2. Molecular structure of the complex $[\overline{\mathrm{Pt}\{\mathrm{CH(CO_2Me)CO}}\bar{\mathrm{C}}\mathrm{(CO_2Me)}\overline{\mathrm{C}}\mathrm{=\overset{+}{N}HBu^t\}(CNBu^t)_2}]$ (**4a**), with only the hydrogens H(3) and H(4) included

positive charge on nitrogen. The zwitterionic complex (**4a**) is a highly planar system as indicated in Table 6. It is also noteworthy that the t-butyl isocyanide ligand *trans* to the dipolar ion fragment is a little bent, with the angle C(2)–N(2)–C(21) being 171.0(7)°. The C(1)–N(1)–C(11) angle of the other ligand is 177.0(7)°. Comparison of the spectroscopic properties of the complexes (**4a**) and (**4b**) indicates that (**4b**) has an analogous structure to (**4a**).

Treatment of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2}]$ (**2b**) with 2 mole equivalents of t-butyl isocyanide, or $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(PPh_3)}]$ (**3b**) with 1 mole equivalent of t-butyl isocyanide in refluxing dichloromethane afforded the zwitterionic complex (**4c**), identified by comparison with the spectroscopic properties of the complexes (**4a**) and (**4b**), Tables 7 and 8.

A possible mechanism for the formation of these zwitterionic complexes based on the above displacement reactions is outlined in the Scheme. The generation of the monosubstituted t-butyl isocyanide platinacyclobutan-3-one ring complex is followed by 'insertion' of a second molecule of t-butyl isocyanide into one of the platinum–carbon σ bonds. This 'insertion' reaction may proceed *via* platinum–carbon bond cleavage followed by attack of the carbon fragment upon a co-ordinated isocyanide. However, details such as whether this is a concerted process or whether the first or second molecule of t-butyl isocyanide is involved in the insertion reaction are not known. Finally, a concerted [1,3]-proton shift (sigmatropic rearrangement)[11] could account for the formation of the zwitterionic complex and its observed stereochemistry. The remaining tertiary-arsine or -phosphine ligand can then be easily substituted with a third molecule of t-butyl isocyanide. All the complexes (**4**) are air-stable, white crystalline solids. Complexes (**4a**) and (**4b**) are slightly soluble in water, to the extent that their ^{1}H n.m.r. spectra can be recorded in D_2O.



Scheme. R = Me or OMe; R′ = Bu^t

The ^{1}H n.m.r. spectra of the complexes (**4**) (Table 7) exhibit a broad low-field signal due to the acidic proton attached to the positively charged nitrogen. These protons couple to the ^{195}Pt nucleus and are readily exchanged on shaking with alkaline D_2O. The NH proton in the triphenylphosphine complex (**4c**) also couples to phosphorus [^4J(PH) 15.6 Hz], the magnitude of this coupling suggesting that phosphorus is *trans* to the C=N bond. The PtCH protons appear in similar positions to those found for the parent complexes (**2**) and show large ^{195}Pt couplings [^2J(PtH) 73—91 Hz]. In the complex (**4c**) there is additional coupling to the phosphorus ligand [^3J(PH) 13.1 Hz], Table 7.

The ^{13}C-{^{1}H} n.m.r. spectra for the complexes (**4**) were fully assigned and selected data are given in Table 7. The isocyanide carbons appear as weak signals in the region δ 131—128 p.p.m.[12,13] The signals at around δ 175 and 169 p.p.m. are assigned to the ester carbonyls. For the acetyl complex (**4b**)

Table 7. ^1H and ^{13}C-{^1H} n.m.r. data for the complexes [$Pt(CHRCO\bar{C}RC{=}\overset{+}{N}HBu^t)(CNBu^t)L$] (**4**)[a]

Complex	δ($\overset{+}{N}H$)	^3J(PtH)	^4J(PH)	δ(CH)	^2J(PtH)	^3J(PH)	δ(CN)	^1J(PtC)	δ(CN)	^1J(PtC)	δ(CO)[b]	^2J(PtC)
(**4a**)	11.17	97.2		3.72	83.2		131.05	*c*	128.24	*c*	175.23	52.3
(**4b**)	13.17	91.0		4.22	90.9		130.22	1 125	128.87	1 017	207.85	39.7
(**4c**)	11.11	104.0	15.6	3.20	73.8	13.1	*d*				175.31	51.1

Complex	δ(CO)[b]	^3J(PtC)	^4J(PC)	δ($C\overset{+}{N}$)	^1J(PtC)	^2J(PC)	δ($\bar{C}$)	^2J(PtC)	δ(CO)$_{ring}$	^2J(PtC)	^3J(PC)	δ(CH)	^1J(PtC)	^2J(PC)
(**4a**)	169.44	68.5		195.75	950.3		109.95	62.3	195.33	*c*		48.6	479.1	
(**4b**)	196.58	61.9		193.95	936.1		120.93	51.8	198.67	12.7		63.6	458.2	
(**4c**)	169.16	*c*	6.0	203.28	*c*	116.3	109.92	*c*	194.09	*c*	6.1	55.3	484.0	6.8

[a] Chemical shifts in p.p.m. relative to $SiMe_4$, coupling constants in Hz. [b] Carbonyl of either ester or acetyl functional groups. [c] Not discernible. [d] Not assignable due to overlapping with phenyl signals.

Table 8. Characteristic i.r. data for the complexes [$Pt(CHRCO\bar{C}RC{=}\overset{+}{N}HBu^t)(CNBu^t)L$] (**4**)*

Complex	R	L	ν($\overset{+}{N}H$)	ν(CN)	ν(CO)/($C{=}\overset{+}{N}$)
(**4a**)	OMe	$CNBu^t$	3 246, 3 202, 3 132, 3 052	2 218, 2 186	1 707, 1 689, 1 632, 1 542
(**4b**)	Me	$CNBu^t$	3 200, 3 012	2 220, 2 192	1 652, 1 612, 1 585, 1 535
(**4c**)	OMe	PPh_3	3 248, 3 204, 3 130, 3 050	2 188	1 702, 1 627, 1 589

* All recorded as KBr discs, absorption bands expressed in cm^{-1}.

these resonances occur at 207.85 and 196.58 p.p.m. This assignment for (**4b**) is based upon its proton-coupled spectrum, the acyl carbonyls exhibiting two bond couplings to their nearest-neighbour hydrogens, with the carbon equivalent to C(51) appearing as a quartet and the carbon equivalent to C(31) appearing as a quintet. The ring carbonyl of the complexes (**4**) appears in the region 198.7—194.1 p.p.m., and in the ^{13}C proton-coupled spectrum of (**4b**) it appears as a doublet due to its coupling with the CH ring proton. The CH ring carbons exhibit large J(PtC) couplings of around 484—458 Hz and for the triphenylphosphine complex (**4c**) a small ^2J(PC) coupling of 6.8 Hz is observed, suggesting again that the phosphorus ligand is *trans* to the C=N group, since the C=N carbon signal has a large ^2J(PC) coupling of 116.3 Hz. The ring carbon C(5) in (**4a**) appears at 109.9 p.p.m. and the equivalent carbons in (**4b**) and (**4c**) appear at 120.9 and 109.9 p.p.m. respectively, each exhibiting coupling to ^{195}Pt.

The 'insertion' reactions of t-butyl isocyanide with the platinacyclobutan-3-one complexes (**2**) can be contrasted with the reaction of t-butyl isocyanide with the platinacyclobutane complex [$Pt(CH_2CH_2CH_2)(bipy)$][6] which leads to displacement of the bipyridyl ligand only to give [$Pt(CH_2CH_2CH_2)(CNBu^t)_2$]. Further differences between these two types of platinacycles are also found in their reactions with carbon monoxide. Thus, although treatment of [$Pt(CH_2CH_2CH_2)L_2$] (L = tertiary phosphine) with carbon monoxide affords the insertion complexes [$Pt\{C(O)CH_2CH_2CH_2\}L_2$],[6] we find that passage of carbon monoxide through a refluxing solution of (**2b**) in dichloromethane or benzene affords only unchanged starting material. Under more vigorous conditions a solution of (**2b**) in benzene at 80 °C under 90 lbf in^{-2} of carbon monoxide afforded the cluster [$Pt_4(CO)_5(PPh_3)_3$][14] in high yield. We also find that there is no reaction between carbon monoxide and the monoisocyanide complex (**3b**) in refluxing benzene.

In conclusion we also note that our attempts to generate platinum(IV) or palladium(IV) metallacyclobutan-3-ones have not been successful. Thus there is no reaction between iodomethane and the complexes [$M\{CH(CO_2Me)COCH(CO_2Me)\}L_2$] (M = Pt, L = PPh_3; M = Pd, L_2 = bipy) at room temperature and treatment of (**2b**) with iodomethane at 60—65 °C results in a complex mixture from which only methyltriphenylphosphonium iodide could be isolated. Treatment of [$Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2$] with either chlorine or iodine afforded the corresponding dihalide complexes [$PtCl_2(PPh_3)_2$] and [$PtI_2(PPh_3)_2$] respectively.

Experimental

The microanalyses were carried out by either C.H.N. Analysis Ltd., South Wigston, Leicester or Butterworth Laboratories Ltd., Teddington, Middlesex. M.p.s were recorded on a Reichart hot-stage apparatus and are uncorrected. A Perkin-Elmer 580 spectrophotometer was used to record i.r. spectra as KBr discs. The ^1H n.m.r. spectra were recorded in $CDCl_3$ at room temperature unless otherwise stated, on either Varian EM390, JEOL JNM-PS-100, or Bruker WH-400 spectrometers operating at 90, 100, and 400 MHz respectively. Chemical shifts are reported relative to internal $SiMe_4$ (0.0 p.p.m.) with positive values to high frequency (low field). The ^{13}C-{^1H} and ^{13}C n.m.r. spectra were recorded in $CDCl_3$ at room temperature on a Bruker WH-400 spectrometer operating at 100 MHz. Carbon-13 chemical shifts are reported relative to internal $SiMe_4$ (0.0 p.p.m.) with positive values to high frequency (low field). The ^{31}P-{^1H} n.m.r. spectra were recorded in dichloromethane at room temperature on a JEOL JNM-FX60 spectrometer operating at 24 MHz. Phosphorus-31 chemical shifts are reported relative to external [$P(OH)_4$]$^+$ in D_2O (0.0 p.p.m.) with positive values to high frequency (low field).[15]

Experiments were performed under a dry, oxygen-free, nitrogen atmosphere, unless otherwise stated, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction boiling in the range 40—60 °C. The metallacyclobutan-3-ones were prepared as described in the literature.[2,3]

Attempted Oxidative Addition Reactions to Metallacyclobutan-3-ones.—(a) *With iodomethane.* (*i*) A solution of [$Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2$] (**2b**) (0.274 g, 0.307 mmol) in dichloromethane (20 cm^3) with iodomethane (0.5 cm^3) was stirred for 24 h. The resulting mixture was evaporated under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (3—5 cm^3) followed by addition of diethyl ether (50 cm^3) gave, after standing (*ca.* 2 h), a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as the starting material [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (0.255 g, 81.8%).

(*ii*) A suspension of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (**2h**) (0.200 g, 0.460 mmol) in dichloromethane (10 cm^3) with iodomethane (1 cm^3) was stirred for 48 h. The yellow microcrystalline solid was filtered off, dried *in vacuo* at 40 °C, and identified as the starting material [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (0.14 g, 70%).

(*iii*) An excess of iodomethane (1 cm^3) was condensed (−196 °C) onto a suspension of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.330 g, 0.370 mmol) in benzene (10 cm^3), contained in a Carius tube. The tube was sealed, shaken at 60—65 °C for 100 h, cooled, and opened. A pale yellow solid was collected and recrystallised from hot water to give, on standing (*ca.* 4 h), white crystals of methyltriphenylphosphonium iodide (0.08 g, 53.5%) identified by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[16]

(b) *With halogens.* (*i*) A slow stream of chlorine was passed through a solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.10 g, 0.11 mmol) in dichloromethane (5 cm^3) for 15 s. Addition of light petroleum (30 cm^3) afforded a yellow solid which was recrystallised from dichloromethane–hexane to give yellow microcrystals of a mixture of (0.09 g, 100%) *cis*- and *trans*-[PtCl$_2$(PPh$_3$)$_2$], identified by comparison of its i.r. spectrum with authentic samples.[17]

(*ii*) A mixture of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.42 g, 0.47 mmol) and iodine (0.12 g, 0.47 mmol) in dichloromethane (40 cm^3) was stirred until a clear pale yellow solution was obtained. The solution was evaporated under reduced pressure to 5 cm^3 volume. Addition of diethyl ether (30 cm^3) gave a yellow solid, which was dried *in vacuo* and identified as [PtI$_2$(PPh$_3$)$_2$] (0.22 g, 48%) by comparison of its i.r. spectrum with an authentic sample.[18]

Substitution Reactions of Metallacyclobutan-3-*ones*.—(*i*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (**2a**) (0.20 g, 0.20 mmol) in dichloromethane (20 cm^3) with triphenylphosphine (0.21 g, 0.80 mmol) was refluxed for 16 h. The resulting mixture was evaporated to dryness under reduced pressure and the residue was recrystallised from dichloromethane–hexane to give a white microcrystalline solid, which was dried *in vacuo* and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.16 g, 90%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[2]

(*ii*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.25 g, 0.26 mmol) in dichloromethane (20 cm^3) with methyldiphenylphosphine (0.15 g, 0.75 mmol) was refluxed for 16 h. The resulting mixture was evaporated to an oil under reduced pressure and the residue was recrystallised from dichloromethane–diethyl ether to give a white microcrystalline solid, which was dried *in vacuo* and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PMePh$_2$)$_2$] (**2c**) (0.16 g, 80%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[2]

(*iii*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.20 g, 0.20 mmol) in dichloromethane (20 cm^3) with dimethylphenylphosphine (0.10 g, 0.72 mmol) was stirred at room temperature for 2 h. The resulting mixture was evaporated to an oil under reduced pressure and the residue was recrystallised from dichloromethane–diethyl ether to give a white microcrystalline solid, which was dried *in vacuo* and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PMe$_2$Ph)$_2$] (**2d**) (0.05 g, 39%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[2]

(*iv*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.35 g, 0.36 mmol) in dichloromethane (40 cm^3) with 1,2-bis(diphenylphosphino)ethane (dppe) (0.15 g, 0.38 mmol) was refluxed for 16 h. The resulting mixture was evaporated to dryness under reduced pressure and the residue was recrystallised from dichloromethane–diethyl ether to give a white microcrystalline solid, which was dried *in vacuo* and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(dppe)] (**2e**) (0.27 g, 98%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[2]

(*v*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.39 g, 0.40 mmol) in dichloromethane (40 cm^3) with 2,2′-bipyridine (0.10 g, 0.64 mmol) was refluxed for 24 h. The solvent was evaporated off under reduced pressure to a volume of 2 cm^3, addition of diethyl ether gave a white microcrystalline solid, which was recrystallised from dichloromethane–hexane, dried *in vacuo*, and identified as the starting material [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.36 g, 92%).

(*vi*) A suspension of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (**2h**) (0.10 g, 0.23 mmol) in dichloromethane (20 cm^3) with triphenylphosphine (0.15 g, 0.57 mmol) was refluxed for 30 min. Cooling, with the addition of diethyl ether (40 cm^3) gave, on standing (*ca.* 2 h), a white microcrystalline solid, which was dried *in vacuo* and identified as [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2g**) (0.16 g, 87%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[3]

(*vii*) A solution of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (**2f**) (0.10 g, 0.11 mmol) in dichloromethane (20 cm^3) with triphenylphosphine (0.10 g, 0.38 mmol) was refluxed for 2 h. The resulting mixture was evaporated to dryness under reduced pressure and the residue was recrystallised from dichloromethane–light petroleum to give a white microcrystalline solid, which was dried *in vacuo* and identified as [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2g**) (0.09 g, 100%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[3]

(*viii*) A suspension of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (**2h**) (0.20 g, 0.46 mmol) in dichloromethane (30 cm^3) with triphenylarsine (0.48 g, 1.57 mmol) was refluxed for 16 h. The addition of light petroleum gave an off-white microcrystalline solid, which was dried *in vacuo* and identified as the starting material [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (0.20 g, 100%).

(*ix*) A solution of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$] (0.20 g, 0.22 mmol) in dichloromethane (30 cm^3) with 2,2′-bipyridine (0.06 g, 0.38 mmol) was refluxed for 16 h. The solvent was evaporated under reduced pressure to a volume of 5 cm^3, addition of light petroleum gave a yellow microcrystalline solid, which was dried *in vacuo* and identified as [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)] (**2h**) (0.09 g, 94%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[3]

(*x*) A solution of [Pt{CH(COMe)COCH(COMe)}(AsPh$_3$)$_2$] (0.35 g, 0.37 mmol) in dichloromethane (40 cm^3) with triphenylphosphine (0.25 g, 0.95 mmol) was stirred at room temperature for 16 h. The solvent was evaporated under reduced pressure to a volume of 5 cm^3, addition of diethyl ether gave a yellow microcrystalline solid, which was recrystallised from dichloromethane–light petroleum, dried *in vacuo*, and identified as $[\mathrm{Pt\{CH(COMe)COCH(COMe)\}(PPh_3)_2}]$ (0.29 g, 91%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[4]

Reactions of Metallacyclobutan-3-*ones with t-Butyl Isocyanide.*—*Using* 1 *mol of t-butyl isocyanide.* (*i*) A solution of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2}]$ (**2a**) (0.500 g, 0.510 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.046 g, 0.553 mmol) was refluxed for 1 h. The resulting clear solution was stirred for 16 h at room temperature and then evaporated under reduced pressure to afford an oil. Dissolution of the oil in dichloromethane (1—2 cm^3) followed by the addition of light petroleum (*ca.* 20 cm^3) gave, after standing for 16 h, a white microcrystalline solid which was dried *in vacuo* at 40 °C and identified as $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)}]$ (**3a**) (0.35 g, 90.6%) (Found: C, 47.90; H, 4.40; N, 1.85. $\mathrm{C_{30}H_{32}AsNO_5Pt}$ requires C, 47.65; H, 4.25; N, 1.85%), m.p. 176—179 °C. N.m.r.: ^{1}H (400 MHz), δ 7.45—7.25 (m, 15 H, Ph), 4.44 [s, 1 H, CH, ^{2}J(PtH) 88.7], 3.90 [s, 1 H, CH, ^{2}J(PtH) 49.3], 3.67 (s, 3 H, Me), 2.94 (s, 3 H, Me), and 1.15 (s, 9 H, $\mathrm{Bu^t}$); ^{13}C-{^{1}H}, 179.77 [s, C=O (ring), ^{2}J(PtC) 189.4], 173.11 [s, C=O, $\mathrm{CO_2Me}$, ^{2}J(PtC) 31.3], 171.68 [s, C=O, $\mathrm{CO_2Me}$, ^{2}J(PtC) 52.6], 132.92 (s, Ph, $\mathrm{C^{\beta}}$), 132.62 (s, Ph, $\mathrm{C^{\alpha}}$), 130.32 (s, Ph, $\mathrm{C^{\delta}}$), 128.80 (s, Ph, $\mathrm{C^{\gamma}}$), 57.67 (s, $\mathrm{Bu^t}$, C), 50.73 (s, Me, $\mathrm{CO_2Me}$), 49.95 (s, Me, $\mathrm{CO_2Me}$), 48.76 [s, CH, ^{1}J(PtC) 288.8], 48.24 [s, CH, ^{1}J(PtC) 267.7 Hz], and 29.49 p.p.m. (s, Me, $\mathrm{Bu^t}$).

(*ii*) A solution of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2}]$ (**2b**) (0.500 g, 0.560 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.047 g, 0.565 mmol) was refluxed for 1 h. The resulting clear solution was stirred for 16 h at room temperature and then evaporated under reduced pressure to afford an oil. Dissolution of the oil in dichloromethane (1—2 cm^3) followed by addition of diethyl ether (30 cm^3) gave, after standing for 16 h, a white microcrystalline solid which was dried *in vacuo* at 40 °C and identified as $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(PPh_3)}]$ (**3b**) (0.34 g, 85.2%) (Found: C, 50.45; H, 4.50; N, 1.90. $\mathrm{C_{30}H_{32}NO_5PPt}$ requires C, 50.55; H, 4.55; N, 1.95%), m.p. > 300 °C. N.m.r.: ^{1}H (400 MHz), δ 7.60—7.25 (m, 15 H, Ph), 4.46 [d, 1 H, CH, ^{3}J(PH) 11.5, ^{2}J(PtH) 71.8], 3.70 (s, 3 H, Me), 3.69 [d, 1 H, CH, ^{3}J(PH) 4.8, ^{2}J(PtH) 46.0], 3.00 (s, 3 H, Me), and 1.16 (s, 9 H, $\mathrm{Bu^t}$); ^{13}C-{^{1}H} 179.63 [d, C=O (ring), ^{3}J(PC) 5.8, ^{2}J(PtC) 177], 173.52 [s, C=O, $\mathrm{CO_2Me}$, ^{2}J(PtC) 25.8], 171.73 [s, C=O, $\mathrm{CO_2Me}$, ^{2}J(PtC) 55.0], 133.76 [d, Ph, $\mathrm{C^{\beta}}$, ^{2}J(PC) 9.1], 131.15 [d, Ph, $\mathrm{C^{\alpha}}$, ^{1}J(PC) 53.4], 130.77 (s, Ph, $\mathrm{C^{\delta}}$), 128.41 [d, Ph, $\mathrm{C^{\gamma}}$, ^{3}J(PC) 10.7], 57.90 (s, C, $\mathrm{Bu^t}$), 51.31 [d, CH, ^{2}J(PC) 2, ^{1}J(PtC) 293], 50.96 [d, CH, ^{2}J(PC) 54.1, ^{1}J(PtC) 216.5], 50.75 (s, Me, $\mathrm{CO_2Me}$), 50.19 (s, Me, $\mathrm{CO_2Me}$), and 29.55 (s, Me, $\mathrm{Bu^t}$); ^{31}P-{^{1}H} 15.1 p.p.m. (s, ^{1}J(PtP) 2 920 Hz).

(*iii*) A solution of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2}]$ (**2f**) (0.500 g, 0.561 mmol) in dichloromethane (50 cm^3) with t-butyl isocyanide (0.048 g, 0.577 mmol) was stirred for 16 h at room temperature. The resulting clear solution was evaporated under reduced pressure to afford an oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of diethyl ether (50 cm^3) gave, after standing for 16 h, a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(AsPh_3)}]$ (**3c**) (0.33 g, 88.1%) (Found: C, 53.90; H, 4.90; N, 2.05. $\mathrm{C_{30}H_{32}AsNO_5Pd}$ requires C, 53.95; H, 4.85; N, 2.10%), m.p. 169—180 °C (decomp.). N.m.r.: ^{1}H (100 MHz, 25—90 °C), δ 7.39 (s, 15 H, Ph), 4.64 (s, 1 H, CH), 4.02 (s, 1 H, CH), 3.70 (s, 3 H, Me, $\mathrm{CO_2Me}$), 2.93 (s, 3 H, Me, $\mathrm{CO_2Me}$), and 1.23 p.p.m. (s, 9 H, Me, $\mathrm{Bu^t}$); ^{1}H (100 MHz, $\mathrm{CD_2Cl_2}$, −95 °C), identical to high temperature spectrum.

(*iv*) A solution of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2}]$ (**2g**) (0.500 g, 0.560 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.053 g, 0.637 mmol) was stirred for 16 h at room temperature. The resulting clear solution was worked up as described in the previous reaction. A white microcrystalline solid was identified as $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(PPh_3)}]$ (**3d**) (0.33 g, 84.9%) (Found: C, 57.60; H, 5.20; N, 2.15. $\mathrm{C_{30}H_{32}NO_5PPd}$ requires C, 57.65; H, 5.15; N, 2.25%), m.p. 175 °C (decomp.). N.m.r.: ^{1}H (90 MHz), δ 7.4—7.3 (m, 15 H, Ph), 4.62 [d, 1 H, CH, ^{3}J(PH) 11.4], 3.79 [d, 1 H, CH, ^{3}J(PH) 6.0], 3.69 (s, 3 H, Me, $\mathrm{CO_2Me}$), 2.97 (s, 3 H, Me, $\mathrm{CO_2Me}$), and 1.20 (s, 9 H, Me, $\mathrm{Bu^t}$); ^{13}C-{^{1}H} 175.2 [d, C=O (ring), ^{3}J(PC) 5.6], 172.85 (s, C=O, $\mathrm{CO_2Me}$), 170.52 (s, C=O, $\mathrm{CO_2Me}$), 133.66 [d, Ph, $\mathrm{C^{\beta}}$, ^{2}J(PC) 12.4], 131.50 [d, Ph, $\mathrm{C^{\alpha}}$, ^{1}J(PC) 41.9], 130.60 (s, Ph, $\mathrm{C^{\delta}}$), 128.59 [d, Ph, $\mathrm{C^{\gamma}}$, ^{3}J(PC) 10.5], 56.90 (s, CH), 56.32 (s, C, $\mathrm{Bu^t}$), 55.74 [d, CH, ^{2}J(PC) 49.2 Hz], 50.74 (s, Me, $\mathrm{CO_2Me}$), 50.10 (s, Me, $\mathrm{CO_2Me}$), and 29.60 (s, Me, $\mathrm{Bu^t}$); ^{31}P-{^{1}H} 23.6 p.p.m. (s).

Using 2 *mol of t-butyl isocyanide.* (*i*) A solution of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2}]$ (**2b**) (0.400 g, 0.448 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.076 g, 0.914 mmol) was refluxed for 1.5 h. The resulting clear solution was stirred for 16 h at room temperature and then evaporated under reduced pressure to afford an oil. Dissolution of the oil in dichloromethane (1—2 cm^3) followed by the addition of diethyl ether (30 cm^3) gave, after standing for 16 h, a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as $[\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C{=}\overset{+}{N}HBu^t\}(CNBu^t)(PPh_3)}]$ (0.28 g, 78.5%) (Found: C, 52.55; H, 5.15; N, 3.45. $\mathrm{C_{35}H_{41}N_2O_5PPt}$ requires C, 52.85; H, 5.20; N, 3.50%), m.p. 165—168 °C. N.m.r.: ^{1}H (400 MHz), 11.11 [d, 1 H, $\overset{+}{\mathrm{N}}$H, ^{4}J(PH) 15.6, ^{3}J(PtH) 104.0], 7.56, 7.51 (m, 6 H, Ph), 7.40, 7.36 (m, 9 H, Ph), 3.68 (s, 3 H, Me, $\mathrm{CO_2Me}$), 3.20 [d, 1 H, CH, ^{3}J(PH) 13.1, ^{2}J(PtH) 73.8], 3.18 (s, 3 H, Me, $\mathrm{CO_2Me}$), 1.51 (s, 9 H, Me, $\mathrm{Bu^t}$), and 0.86 (s, 9 H, Me, $\mathrm{Bu^t}$); ^{13}C-{^{1}H} 203.28 [d, $\mathrm{C{=}\overset{+}{N}}$, ^{2}J(PC) 116.3], 194.09 [d, C=O (ring), ^{3}J(PC) 6.1], 175.31 [s, C=O (ester), ^{2}J(PtC) 51.1], 169.16 [d, C=O (ester), ^{4}J(PC) 6.0], 134.27 [d, Ph, $\mathrm{C^{\beta}}$, ^{2}J(PC) 11.5], 130.74 (s, Ph, $\mathrm{C^{\delta}}$), 130.39 [d, Ph, $\mathrm{C^{\alpha}}$, ^{1}J(PC) 52.4], 128.32 [d, Ph, $\mathrm{C^{\gamma}}$, ^{3}J(PC) 10.4], 109.92 (s, $\overset{-}{\mathrm{C}}$), 57.63 (s, C, $\mathrm{Bu^t}$), 55.26 [d, CH, ^{2}J(PC) 6.8, ^{1}J(PtC) 484.0], 54.40 [d, C, $\mathrm{Bu^t}$, ^{4}J(PC) 10.4, ^{3}J(PtC) 62.7], 50.02 (s, Me, $\mathrm{CO_2Me}$), 49.94 (s, Me, $\mathrm{CO_2Me}$), 30.96 (s, Me, $\mathrm{Bu^t}$), and 28.83 (s, Me, $\mathrm{Bu^t}$); ^{31}P-{^{1}H} 16.7 p.p.m. (s, ^{1}J(PtP) 2 026.4 Hz).

(*ii*) A solution of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(CNBu^t)(PPh_3)}]$ (**3b**) (0.300 g, 0.421 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.036 g, 0.433 mmol) was refluxed for 2 h. The resulting clear solution was stirred for 16 h at room temperature and then worked up as described in the previous reaction. A white microcrystalline solid was identified as $[\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C{=}\overset{+}{N}HBu^t\}(CNBu^t)(PPh_3)}]$ (0.14 g, 41.8%) by its i.r. and ^{1}H n.m.r. spectra.

Using 3 *mol of t-butyl isocyanide.* (*i*) A solution of $[\mathrm{Pt\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2}]$ (**2a**) (0.685 g, 0.699 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.175 g, 2.10 mmol) was refluxed for 1.5 h. The resulting clear solution was stirred for 16 h at room temperature and then evaporated under reduced pressure to afford an oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by the addition of diethyl ether (40 cm^3) gave, after standing for 24 h, a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as $[\mathrm{Pt\{CH(CO_2Me)CO\overset{-}{C}(CO_2Me)C{=}\overset{+}{N}HBu^t\}(CNBu^t)_2}]$ (**4a**) (0.38 g, 88.2%) (Found: C, 43.05; H, 5.75; N, 6.80. $\mathrm{C_{22}H_{35}N_3O_5Pt}$ requires C, 42.85; H, 5.70; N, 6.80%), m.p.

141—142 °C. N.m.r.: ^{1}H (400 MHz), δ 11.17 {s, 1 H, $\overset{+}{\mathrm{N}}$H, ^3J(PtH) 97.2, undergoes exchange with D$_2$O–[NaO]$^-$}, 3.72 [s, 1 H, CH, ^2J(PtH) 83.2], 3.59 (s, 3 H, Me, CO$_2$Me), 3.39 (s, 3 H, Me, CO$_2$Me), 1.44 (s, 9 H, Me, Bu^t), 1.39 (s, 9 H, Me, Bu^t), and 1.35 (s, 9 H, Me, Bu^t); ^{13}C-{^{1}H} 195.75 [s, C=$\overset{+}{\mathrm{N}}$, ^1J(PtC) 950.3], 195.33 [s, C=O (ring)], 175.23 [s, C=O (ester), ^2J(PtC) 52.3], 169.44 [s, C=O (ester), ^3J(PtC) 68.5], 131.05 (s, br, C≡N), 128.24 [s, br, C≡N], 109.95 [s, C$^-$, ^2J(PtC) 62.3], 57.99 (s, C, Bu^t), 57.88 (s, C, Bu^t), 53.69 [s, C, Bu^t, ^3J(PtC) 29.2], 50.20 (s, Me, CO$_2$Me), 49.78 (s, Me, CO$_2$Me), 48.64 [s, CH, ^1J(PtC) 479.1 Hz], 30.75 (s, Me, Bu^t), 29.72 (s, Me, Bu^t), and 29.44 p.p.m. (s, Me, Bu^t).

(*ii*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.30 g, 0.34 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.095 g, 1.14 mmol) was refluxed for 2 h. The resulting clear solution was worked up as described in the previous reaction. A white microcrystalline solid was identified as [Pt{CH(CO$_2$Me)CO$\overset{-}{\mathrm{C}}$(CO$_2$Me)C=$\overset{+}{\mathrm{N}}$HBu^t}(CNBu^t)$_2$] (**4a**) (0.18 g, 86%) by its i.r. and ^{1}H n.m.r. spectra.

(*iii*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(AsPh$_3$)] (**3a**) (0.82 g, 1.08 mmol) in dichloromethane (30 cm^3) with t-butyl isocyanide (0.19 g, 2.28 mmol) was refluxed for 1 h. The resulting clear solution was stirred at room temperature for 16 h and then worked up as described in (*i*) above. A white microcrystalline solid was identified as [Pt{CH(CO$_2$Me)CO$\overset{-}{\mathrm{C}}$(CO$_2$Me)C=$\overset{+}{\mathrm{N}}$HBu^t}(CNBu^t)$_2$] (**4a**) (0.52 g, 78%) by its i.r. and ^{1}H n.m.r. spectra.

(*iv*) A solution of [Pt{CH(COMe)COCH(COMe)}(AsPh$_3$)$_2$] (0.403 g, 0.425 mmol) in dichloromethane (50 cm^3) with t-butyl isocyanide (0.110 g, 1.32 mmol) was refluxed for 1 h. The resulting pale yellow solution was stirred for 16 h at room temperature and then worked up as described in reaction (*i*) above. A white microcrystalline solid was identified as [Pt{CH(COMe)CO$\overset{-}{\mathrm{C}}$(COMe)C=$\overset{+}{\mathrm{N}}$HBu^t}(CNBu^t)$_2$] (**4b**) (0.21 g, 84.5%) (Found: C, 45.60; H, 6.45; N, 7.00. C$_{22}$H$_{35}$N$_3$O$_3$Pt requires C, 45.20; H, 6.05; N, 7.20), m.p. 154—156 °C. N.m.r.: ^{1}H (400 MHz), δ 13.17 [s, 1 H, $\overset{+}{\mathrm{N}}$H, ^3J(PtH) 91.0], 4.22 [s, 1 H, CH, ^2J(PtH) 90.9], 2.46 (s, 3 H, Me, COMe), 2.11 (s, 3 H, Me, COMe), 1.60 (s, 9 H, Me, Bu^t), 1.54 (s, 9 H, Me, Bu^t), and 1.51 (s, 9 H, Me, Bu^t); ^{13}C-{^{1}H} 207.85 [s, C=O (acetyl), ^2J(PtC) 39.7, ^2J(HC) 5.8 (qnt from ^{13}C spectrum)], 198.67 [s, C=O (ring), ^2J(PtC) 12.7, ^2J(HC) 3.4 (d from ^{13}C spectrum)], 196.58 [s, C=O (acetyl), ^3J(PtC) 61.9, ^2J(HC) 5.9 (q from ^{13}C spectrum)], 193.95 [s, C=$\overset{+}{\mathrm{N}}$, ^1J(PtC) 936.1, ^2J(HC) 4.3 (d from ^{13}C spectrum)], 130.22 [s, br, C≡N, ^1J(PtC) 1 125], 128.87 [s, br, C≡N, ^1J(PtC) 1 017], 120.93 [s, $\overset{-}{\mathrm{C}}$, ^2J(PtC) 51.82, ^3J(HC) 6.2 (d from ^{13}C spectrum)], 63.59 [s, CH, ^1J(PtC) 458.2, ^1J(HC) 136.0 (d from ^{13}C spectrum)], 58.33 (s, C, Bu^t), 58.21 (s, C, Bu^t), 53.94 [s, C, Bu^t, ^3J(PtC) 29.0 Hz], 30.82 (s, Me, Bu^t), 29.83 (s, Me, Bu^t), 29.60 (s, Me, Bu^t), 29.38 (s, Me, COMe), and 28.75 p.p.m. (s, Me, COMe).

Reactions of [M{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)L].—(*i*) A solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(AsPh$_3$)] (**3a**) (0.289 g, 0.382 mmol) in dichloromethane (10 cm^3) with triphenylphosphine (0.101 g, 0.385 mmol) was stirred for 4 h at room temperature. Addition of light petroleum (50 cm^3) gave a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(PPh$_3$)] (**3b**) (0.25 g, 91.5%) by its i.r. and ^{1}H n.m.r. spectra.

(*ii*) A mixture of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(AsPh$_3$)] (**3a**) (0.360 g, 0.476 mmol) in dichloromethane (30 cm^3) with triphenylphosphine (0.26 g, 0.99 mmol) was refluxed for 2 h. The resulting solution was evaporated under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of diethyl ether (50 cm^3) gave a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.11 g, 25.9%) by comparison of its i.r. and ^{1}H n.m.r. spectra with an authentic sample.[2]

(*iii*) A solution of [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(AsPh$_3$)] (**3c**) (0.200 g, 0.299 mmol) in dichloromethane (30 cm^3) with triphenylphosphine (0.08 g, 0.30 mmol) was stirred for 16 h at room temperature. The resulting solution was worked up as described in the previous reaction. A white microcrystalline solid was identified as [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(PPh$_3$)] (**3d**) (0.12 g, 64.3%) by its i.r. and ^{1}H n.m.r. spectra.

(*iv*) A slow stream of carbon monoxide was passed through a refluxing solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(PPh$_3$)] (**3b**) (0.300 g, 0.421 mmol) in benzene (50 cm^3) for 24 h. The resulting solution was worked up as described in (*ii*) above. A white microcrystalline solid was identified as the starting material [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(PPh$_3$)] (**3b**) (0.297 g, 96.7%).

Miscellaneous Reactions of [Pt{CH(CO$_2$R)COCH(CO$_2$R)}(PPh$_3$)$_2$].—(*i*) A slow stream of carbon monoxide was passed through a refluxing solution of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.40 g, 0.45 mmol) in dichloromethane (80 cm^3) for 24 h. The resulting solution was evaporated under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (1—2 cm^3) followed by addition of diethyl ether (40 cm^3) gave, after standing for 1 h, a white microcrystalline solid which was recrystallised from dichloromethane–light petroleum, dried *in vacuo* at 40 °C, and identified as the starting material (0.38 g, 95%).

(*ii*) A suspension of [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$] (**2b**) (0.40 g, 0.45 mmol) in benzene (25 cm^3) was placed into a steel 'bomb' (200 cm^3). The 'bomb' was placed under a pressure of carbon monoxide (90 lbf in^{-2}), heated to 80 °C for 24 h, cooled, and the pressure released. A deep red solution was removed, evaporated under reduced pressure to a volume of 2 cm^3. Addition of light petroleum gave a brown-red solid, which was dried *in vacuo* at 40 °C, and identified as [Pt$_4$(CO)$_5$(PPh$_3$)$_3$] (0.18 g, 95%) by comparison of its i.r. spectrum with an authentic sample.[14]

X-*Ray Crystal-structure Determinations of the Complexes.*—(*a*) [Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(CNBu^t)(AsPh$_3$)] (**3a**). Crystals of (**3a**) were grown from dichloromethane–light petroleum. A crystal of dimensions *ca.* 0.29 × 0.13 × 0.08 mm was mounted in air. The cell dimensions were determined from an oscillation photograph about the *b* axis of the crystal and from its optimised counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. Intensity data were collected at 293 K on a Stöe Weissenberg diffractometer with an ω scan technique in the range $7 < 2\theta < 55°$. The 3 142 reflections, collected from Weissenberg layers $h(0—11)l$ having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX.[19]

Crystal data. C$_{30}$H$_{32}$AsNO$_5$Pt·H$_2$O, M = 774.3, monoclinic, a = 19.840(3), b = 11.1086(6), c = 28.4880(1) Å, β = 102.96(6)°, U = 6 107.4 Å^3, Z = 8, D_c = 1.68 g cm^{-3}, F(000) = 3 311.5, space group $C2/c$, Mo-K_α X-radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 54.80 cm^{-1}.

Table 9. Fractional atomic co-ordinates for $[\mathrm{Pt}\{\mathrm{CH(CO_2Me)COCH(CO_2Me)}\}(\mathrm{CNBu^t})(\mathrm{AsPh_3})]$ (**3a**)

Atom	*x*	*y*	*z*
Pt	0.074 43(2)	0.201 42(4)	0.134 64(1)
As	−0.044 90(5)	0.155 62(10)	0.100 94(3)
O(1)	0.146 8(4)	0.440 6(8)	0.210 75(29)
O(2)	−0.010 7(5)	0.550 9(10)	0.118 5(4)
O(3)	−0.011 1(4)	0.427 6(9)	0.178 8(3)
O(4)	0.199 1(4)	0.353 3(9)	0.090 23(29)
O(5)	0.254 5(5)	0.189 4(10)	0.124 4(3)
O(6)	0.458 5(10)	0.311 8(22)	0.206 6(7)
N(1)	0.128 8(4)	−0.057 7(8)	0.150 41(29)
C(1)	0.071 3(8)	0.386 5(13)	0.132 2(5)
C(2)	0.135 3(6)	0.387 2(12)	0.172 6(4)
C(3)	0.173 5(5)	0.278 5(11)	0.161 9(4)
C(4)	0.014 0(7)	0.464 7(12)	0.141 8(5)
C(5)	−0.069 9(7)	0.496 3(16)	0.190 7(6)
C(6)	0.208 4(6)	0.279 6(13)	0.121 4(4)
C(7)	0.295 2(8)	0.192 4(17)	0.087 1(6)
C(11)	0.104 5(5)	0.035 9(10)	0.144 2(3)
C(12)	0.166 6(7)	−0.172 4(12)	0.159 6(5)
C(13)	0.147 7(8)	−0.248 1(15)	0.113 4(5)
C(14)	0.246 1(7)	−0.131 7(16)	0.171 1(7)
C(15)	0.142 1(11)	−0.236 3(17)	0.199 8(6)
C(41)	−0.096 5(4)	0.278 1(6)	0.060 76(24)
C(42)	−0.064 0(4)	0.339 7(6)	0.029 28(24)
C(43)	−0.100 8(4)	0.424 8(6)	−0.002 45(24)
C(44)	−0.170 1(4)	0.448 3(6)	−0.002 66(24)
C(45)	−0.202 6(4)	0.386 7(6)	0.028 85(24)
C(46)	−0.165 8(4)	0.301 6(6)	0.060 55(24)
C(51)	−0.097 4(3)	0.121 6(7)	0.149 14(21)
C(52)	−0.073 9(3)	0.169 5(7)	0.195 17(21)
C(53)	−0.109 9(3)	0.145 9(7)	0.231 05(21)
C(54)	−0.169 2(3)	0.074 3(7)	0.220 92(21)
C(55)	−0.192 7(3)	0.026 4(7)	0.174 89(21)
C(56)	−0.156 7(3)	0.050 0(7)	0.139 00(21)
C(61)	−0.063 2(3)	0.014 9(6)	0.060 10(22)
C(62)	−0.044 4(3)	−0.098 1(6)	0.080 13(22)
C(63)	−0.058 6(3)	−0.201 2(6)	0.051 62(22)
C(64)	−0.091 7(3)	−0.191 1(6)	0.003 10(22)
C(65)	−0.110 5(3)	−0.078 1(6)	−0.016 91(22)
C(66)	−0.096 2(3)	0.024 9(6)	0.011 59(22)
H(1)	0.087(4)	0.421(7)	0.105 5(25)
H(3)	0.195(4)	0.237(7)	0.190 2(26)

The structure was solved by conventional Patterson and difference Fourier techniques. Scattering factors were taken from ref. 20. In the final stages of block-matrix least-squares refinement all non-hydrogen atoms were given anisotropic thermal parameters. All the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The hydrogen-atom positions for H(1) and H(3) were located from a difference Fourier map and were refined with isotropic thermal parameters. The hydrogen atom thermal parameters refined to reasonable values. The hydrogen atoms of the phenyl rings and methyl groups were refined at calculated positions [C–H 1.08(5) Å]. Final cycles employed a weighting factor *w* calculated from $w = k/(\sigma^2F + gF^2)$, where $k = 1.55$, $g = 0.000\,21$. Final values of *R* and *R′* are 0.0465 and 0.0405. Fractional atomic co-ordinates are given in Table 9.

(*b*) $[\mathrm{Pt}\{\mathrm{CH(CO_2Me)CO\bar{C}(CO_2Me)C(\overset{+}{N}HBu^t)}\}(\mathrm{CNBu^t})_2]$ (**4a**). Conditions were as for (**3a**) except for the following: crystal size 0.575 × 0.38 × 0.18 mm; intensity data were collected in the range $7 < 2\theta < 50°$ for 6 310 reflections from Weissenberg layers *hk*(0—14); final weighting parameter $k = 0.75$, $g = 0.0042$; final *R* and *R′* values were 0.0422 and 0.0474.

Crystal data. $C_{22}H_{35}N_3O_5Pt{\cdot}CHCl_3$, $M = 735.9$, triclinic, $a = 11.427(3)$, $b = 11.650(1)$, $c = 12.568(6)$ Å, $\alpha = 93.28(1)$, $\beta = 101.97(1)$, $\gamma = 109.66(6)°$, $U = 1\,526.6$ Å^3, $Z = 2$, $D_c = 1.60$ g cm^{-3}, *F*(000) 713.91, space group $P\bar{1}$, $\mu(\text{Mo-}K_\alpha) = 46.81$ cm^{-1}.

Table 10. Fractional atomic co-ordinates for $[\mathrm{Pt}\{\mathrm{CH(CO_2Me)CO\bar{C}(CO_2Me)C(\overset{+}{N}HBu^t)}\}(\mathrm{CNBu^t})_2]$ (**4a**)

Atom	*x*	*y*	*z*
Pt	0.222 21(2)	0.056 38(2)	0.128 30(2)
Cl(1)	0.251 2(4)	0.430 1(3)	0.639 7(3)
Cl(2)	0.331 9(5)	0.433 1(6)	0.873 2(4)
Cl(3)	0.195 7(4)	0.587 5(3)	0.789 6(4)
O(31)	0.379 1(6)	−0.159 4(6)	0.185 3(5)
O(6)	0.025 2(5)	−0.283 3(5)	0.158 6(4)
O(32)	0.331 9(5)	−0.160 0(5)	0.001 8(4)
O(51)	0.198 7(6)	−0.098 6(5)	0.482 6(4)
O(52)	0.090 9(6)	−0.278 8(5)	0.380 7(4)
N(1)	0.219 5(6)	0.321 9(5)	0.171 2(5)
N(2)	0.183 9(6)	0.044 5(6)	−0.126 4(4)
N(41)	0.321 0(5)	0.081 1(5)	0.380 6(4)
C(1)	0.229 2(6)	0.227 8(6)	0.158 6(5)
C(2)	0.189 8(7)	0.058 4(6)	−0.033 5(6)
C(3)	0.184 3(6)	−0.132 9(5)	0.094 6(5)
C(11)	0.213 6(8)	0.446 2(6)	0.185 9(7)
C(5)	0.167 4(5)	−0.109 4(5)	0.289 5(4)
C(14)	0.116 3(15)	0.453 7(12)	0.088 5(10)
C(13)	0.350 4(11)	0.535 6(9)	0.198 7(12)
C(4)	0.249 7(5)	0.012 6(5)	0.286 2(5)
C(7)	0.211 6(9)	0.445 1(9)	0.769 2(9)
C(21)	0.172 2(7)	0.006 4(6)	−0.242 8(5)
C(22)	0.280 0(10)	−0.040 8(13)	−0.246 4(7)
C(23)	0.180 0(14)	0.119 7(12)	−0.303 0(9)
C(12)	0.165 7(14)	0.457 3(11)	0.292 6(10)
C(31)	0.306 3(7)	−0.153 1(5)	0.102 5(5)
C(24)	0.041 1(11)	−0.094 0(12)	−0.289 5(11)
C(6)	0.116 3(6)	−0.184 8(5)	0.183 4(5)
C(32)	0.450 0(9)	−0.174 7(10)	−0.003 2(8)
C(41)	0.434 0(6)	0.196 1(6)	0.407 8(6)
C(42)	0.396 0(11)	0.306 1(8)	0.432 5(10)
C(43)	0.523 9(9)	0.178 4(9)	0.510 8(9)
C(44)	0.507 5(8)	0.216 7(10)	0.315 9(10)
C(51)	0.155 0(6)	−0.157 7(5)	0.391 1(5)
C(52)	0.088 5(12)	−0.332 3(9)	0.482 4(8)
H(3)	0.131(5)	−0.161(5)	0.025(4)
H(4)	0.317(6)	0.065(6)	0.453(6)

Fractional atomic co-ordinates are given in Table 10.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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