Acetylenes and Noble-metal Compounds. Part 14.[1] Insertion Reactions of 6-Chloro-2,2,4,5,7,7-hexamethylocta-3,5-dien-3-ylpalladium Compounds; the $PdCl_2$-catalysed Carbonylation of Acetylenes to Cyclopentadienones

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Carbonylation of the kinetically favoured σ-butadienyl complex [Pd(CBu^t=CMeCMe=CBu^{t}Cl)(bipy)Cl] (2; bipy = 2,2′-bipyridyl) gives an insoluble complex (6) which is suggested to be [Pd{η^3-CBu^t=CMeCMe=C(Bu^t)(Cl)C=O}-Cl}$_n$]. Complex (6) on heating or on treatment with trimethyl phosphite gives 3,4-dimethyl-2,5-di-t-butylcyclopentadienone (4) which could also be obtained catalytically by carbonylation of Bu^{t}C$_2$Me in the presence of [Pd(NCPh)$_2$Cl$_2$]. Complex (6) reacts with pyridine (py) to give the exocyclic η^3-allylic complexes [Pd$_2$-{η^3-CH$_2$···C···CBu^{t}C(=O)CBu^t=CMe}$_2$Cl$_2$] and [Pd{η^3-CH$_2$···C···CBu^{t}C(=O)CBu^t=CMe}(py)Cl], which with HCl generates (4). The acetylenes PhC$_2$Ph and PhC$_2$Bu^t are also carbonylated catalytically in the presence of [Pd(NCPh)$_2$Cl$_2$] to tetraphenylcyclopentadienone and 3,4-diphenyl-2,5-di-t-butylcyclopentadienone respectively. A new mechanism for the formation of cyclopentadienones *via* σ-butadienylpalladium complexes is proposed. The σ,π-butadienyl complex [Pd$_3$(η^3-CBu^t=CMeCMe=CBu^{t}Cl)$_2$Cl$_4$] reacts with mono-t-butyl-acetylene to give 1,3-dimethyl-2,4,6-tri-t-butylbenzene, a result which agrees with previous proposals for the mechanism of acetylene cyclotrimerisation reactions. The bipy ligand in complex (2) and in its thermodynamically favoured isomer (3) is labile and can be transferred to MCl$_2$ to give [M(bipy)Cl$_2$] (M = Pd or Pt) and [Pd$_2$(CBu^t=CMeCMe=CBu^{t}Cl)$_2$Cl$_2$] which rearranges to the cyclobutadiene complex [Pd$_2$(C$_4$Bu$^t_2$Me$_2$)$_2$Cl$_4$].

ALTHOUGH the co-dimerisation of two acetylenes with one carbon monoxide to give cyclopentadienone is a well established reaction promoted by many metal carbonyls,[2-4] it does not appear to have been reported previously for palladium which, although very active as a carbonylation catalyst, forms few well characterised simple carbonyl complexes, particularly in low oxidation states.[5] Furthermore, only a few reactions have been reported in which cyclopentadienones are formed catalytically.[3] This is perhaps not surprising since cyclopentadienones without bulky substituents are highly reactive (and tend to dimerise [6]) and since they form strong complexes to metals.[2]

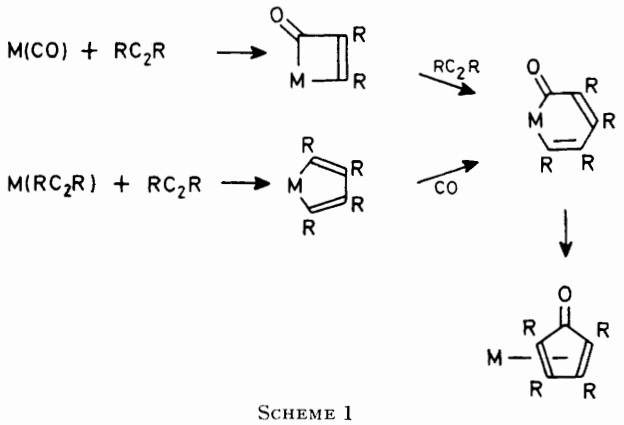
Although the mechanisms by which cyclopentadienones and their complexes are formed by co-dimerisation of two acetylenes and CO have not been investigated in any detail, reaction schemes such as that shown (Scheme 1) are probable for reactions occurring at a single metal atom where the metal can undergo ready two-electron oxidative addition, reductive-elimination, reactions (*e.g.* $Fe^0 \rightleftharpoons Fe^{II}$, $Co^I \rightleftharpoons Co^{III}$, and $Rh^I \rightleftharpoons Rh^{III}$).[2,4,7]

We here report on the formation of cyclopentadienones by carbonylation of σ-butadienylpalladium complexes as well as directly from acetylenes and carbon monoxide. These reactions are examples of a hitherto unsuspected route to cyclopentadienones.

RESULTS AND DISCUSSION

Carbonylation of 6-Chloro-2,2,4,5,7,7-hexamethylocta-3,5-dien-3-ylpalladium Complexes.—In the preceding paper we have reported [1] on the $PdCl_2$-induced dimerisation of 4,4-dimethylpent-2-yne [t-butyl(methyl)-acetylene, bma] to the σ-butadienylpalladium complex (1). This was characterised by reaction with 2,2′-bipyridyl (bipy) which gave the labile but kinetically favoured isomer (2) in which the Pd–Cl and the C–Cl are on the same side; (2) readily isomerised to (3), the structure of which was established by *X*-ray analysis which showed the Pd–Cl and the C–Cl to be on opposite sides of the molecule.[8]

Carbonylation (20 °C, 1 atm) * of complex (3) gave



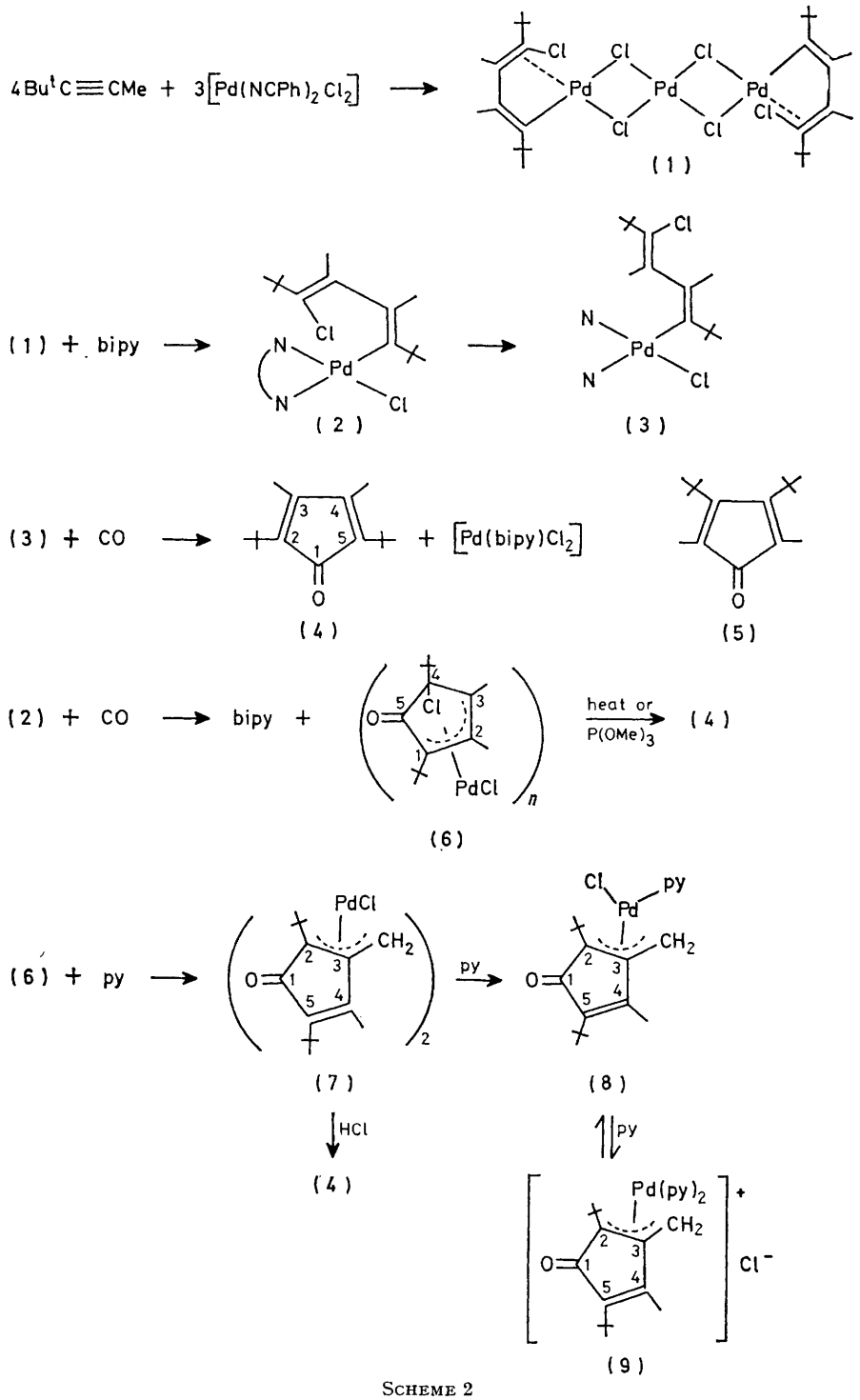
SCHEME 1

only a small amount of an orange-red organic compound, characterised as 3,4-dimethyl-2,5-di-t-butylcyclopentadienone (4) by analysis, mass spectrometry (parent ion at *m/e* 220), and spectroscopically [i.r.: ν(CO) at 1 710 cm^{-1}]. The ^{1}H and the ^{13}C n.m.r. spectra showed the molecule to have a plane of symmetry and we prefer the structure shown to the alternative (5) since it is highly unlikely that the CO has inserted into the middle of the butadienyl chain which is already present in (3).

Carbonylation of the kinetically favoured isomer (2) led to the loss of bipyridyl and the formation of an

* Throughout this paper: 1 atm = 101 325 Pa.

extremely insoluble yellow solid of empirical formula $(C_{15}H_{24}Cl_2OPd)_n$ (6) the i.r. spectrum of which showed the presence of a ketone [ν(CO) at 1 710 cm^{-1}]. Complex (6) was an intermediate in the formation of the cyclopentadienone (4) which could be obtained in high conversion by heating (6) in nitromethane to 100 °C or by the addition of trimethyl phosphite at room temperature, as shown by n.m.r. spectroscopy. However, reaction of (6) with more basic ligands gave quite different products; for example, with 1 equivalent of pyridine (per Pd) a new dimeric complex (7) was obtained which was cleaved by excess of pyridine to give the adduct (8).



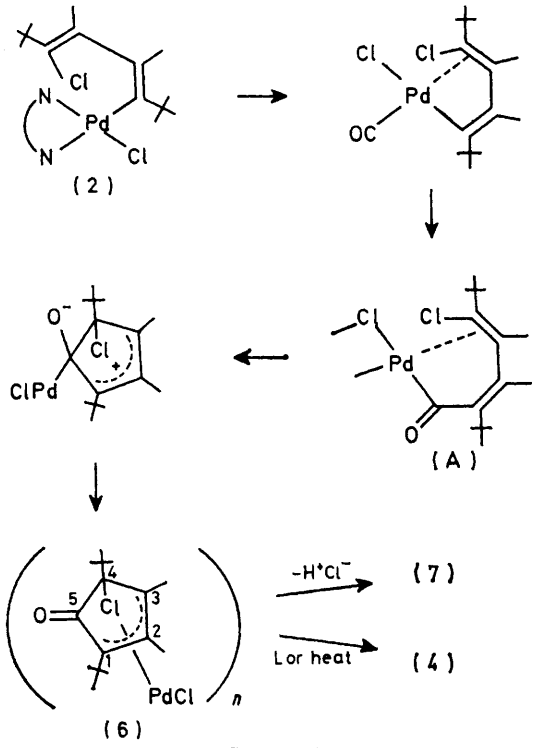
Scheme 2

The ^1H n.m.r. spectra of (7) and (8) both showed the

presence of two closely spaced singlet resonances, due to two t-butyl groups, as well as another singlet arising from *one* methyl. In addition the spectra showed an AB multiplet of intensity corresponding to 2 H. This, taken together with the stoicheiometries of the compounds, suggested that HCl had been lost in the formation of (7) and that the metal was bound to the ligand by an exocyclic η^3-allylic bond. The AB multiplet of intensity 2 must then arise from a $=CH_2$ group and the compounds may be formulated as ' dehydrocyclopentadienone complexes ' as shown. This assignment was confirmed by the ^{13}C n.m.r. spectrum of complex (8) which in particular showed the CH_2 as a triplet at δ 59.9 p.p.m.; other resonances were assigned by comparison with data reported for other exocyclic η^3-allylic palladium complexes.[9] The dimer complex (7) showed ν(Pd–Cl) bands at 254 and 260 cm^{-1} in the far-i.r. spectrum, typical for a Pd_2Cl_2 bridging group, while (8) showed a single strong band at 280 cm^{-1} which we ascribe to a terminal ν(Pd–Cl). Further support for the formulation comes from the observation that both (7) and (8) gave the cyclopentadienone (4) when treated with hydrogen chloride gas. A somewhat related reaction, the loss of HCl from a CH_3–C=C π-bonded to $PdCl_2$, has been reported by Shaw and Shaw.[10]

We also monitored by ^1H n.m.r. spectroscopy the changes which occurred in the reaction of (6) with pyridine. The initial spectrum in pyridine showed two t-butyl (δ 1.07 and 1.46 p.p.m.) and *two* methyl resonances (1.55 and 2.42 p.p.m.); after 30 min, changes became apparent and new peaks were observed. This reaction was complete after 18 h, and the spectrum then showed resonances at δ 1.29 (Bu^t), 1.32 (Bu^t), 2.08 (Me), 4.34, and 4.47 p.p.m. [CH_2, J(H–H) = 2.4 Hz]. The monopyridine adduct (8) could be isolated from this solution but it showed a slightly different ^1H spectrum; it is possible that in pyridine solution (8) gives the ionic species (9) which is that seen in the n.m.r. spectrum. These reactions are summarised in Scheme 2.

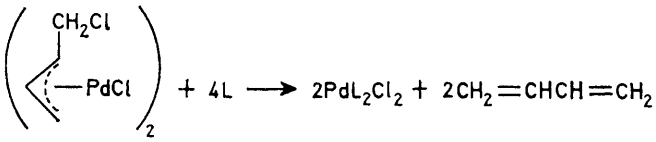
The structure of the insoluble complex (6) is not known with any certainty. It clearly contains a carbonyl group and the initial n.m.r. spectrum in pyridine shows two t-butyl and two methyl groups still to be present and indicates the absence of any symmetry in the organic ligand; the far-i.r. spectrum shows bands at 225m, 260m, and 278s cm^{-1} and is consistent with the presence of bridging PdCl groups. We may postulate that (6) arises from (2) by the replacement of (labile) bipy by a CO, the CO initially attacking at the relatively unshielded sixth co-ordination site of the metal [the fifth site being shielded by the t-butyl on C(3)]. If this intermediate then undergoes insertion * of the co-ordinated carbonyl into the Pd–butadienyl σ-bond then a further intermediate (A) may be formed. This is not likely to be complex (6) since the ν(CO) observed for (6) is much higher than is usually found (1 635—1 675 cm^{-1}) for –CR=CR–CO–M groupings.[4,11] We suggest that the ligand has already cyclised in (6), possibly by a thermally allowed disrotatory ring closure (Scheme 3) and that it has the endocyclic allylic structure shown. In



SCHEME 3

the presence of pyridine, loss of H^+ from the methyl adjacent to the C(Bu^t)Cl together with loss of that chlorine then gives the exocyclic allylic complexes (7) and (8).

This structure also accounts for the formation of the cyclopentadienone (4) on reaction of (6) with non-basic ligands. For example, phosphines and other non-basic ligands cause the loss of $PdCl_2$ and the generation of dienes from 1-chloromethyl-allylic complexes,[12] *e.g.*:



In the case of (6) a similar reaction can also occur on heating.

The thermodynamically favoured bipyridyl complex (3) has the terminal C(Bu^t)Cl shielding the sixth co-ordination site as well as having the Bu^t on C(3) blocking the fifth co-ordination site. Attack by CO will therefore be severely inhibited; furthermore, the conformation of the butadienyl ligand in (3) may well also not favour cyclisation. For these reasons (3) may be expected, and is indeed found, to be more inert than (2).

Separate experiments showed the cyclobutadiene complex [$Pd_2(C_4Bu^t_2Me_2)_2Cl_4$] (13) to be inert to carbon

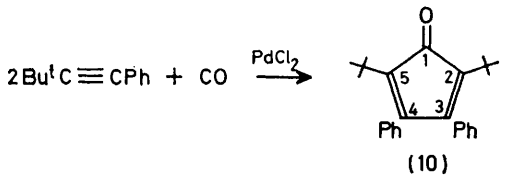
* The term ' insertion ' is used in a descriptive sense here and elsewhere; such reactions are probably examples of alkenyl migrations on to co-ordinated CO.

monoxide and hence suggested that the reaction did proceed *via* a σ-butadienylpalladium intermediate and not by insertion of CO into a complexed cyclobutadiene.

$PdCl_2$-*Catalysed Co-dimerisation of Acetylenes and Carbon Monoxide.*—Since the bipyridyl in (2) plays little role in the reaction of the σ-butadienylpalladium entity with CO, other than to stabilise an intermediate and to hinder its decomposition to a cyclobutadiene complex, the catalytic formation of the cyclopentadienone (4) [*via* complexes (1) and (6)] ought to be possible at elevated temperatures where (6) is not stable.

In fact, when bma was allowed to react with $[Pd(NCPh)_2Cl_2]$ in the presence of carbon monoxide in chlorobenzene at 130 °C, the cyclopentadienone (4) was obtained catalytically in yield corresponding to a turnover number of eight molecules of (4) per Pd. The reason for the relatively low turnover number was found to be due to the formation of the exocyclic allylic complex (7). This represents a chain-termination step in the reaction which is apparently promoted by the high temperature needed for the catalytic carbonylation reaction.

In attempts to circumvent the formation of by-products and also to test the generality of the cyclopentadienone formation reaction, diphenylacetylene and 3,3-dimethyl-1-phenylbut-1-yne [t-butyl(phenyl)-acetylene] were both carbonylated under the same conditions. In neither case should the elimination of HCl to give analogues of (7) be possible. Diphenylacetylene gave tetraphenylcyclopentadienone with a turnover comparable to that for bma; in this case, however, a different competing reaction was found, the cyclotrimerisation of the acetylene to hexaphenylbenzene.[13] t-Butyl(phenyl)acetylene gave the hitherto unreported 3,4-diphenyl-2,5-di-t-butylcyclopentadienone (10), but in lower turnover; presumably in this case the somewhat greater bulk of the phenyl (by comparison with the methyl of bma) slowed the reaction. The



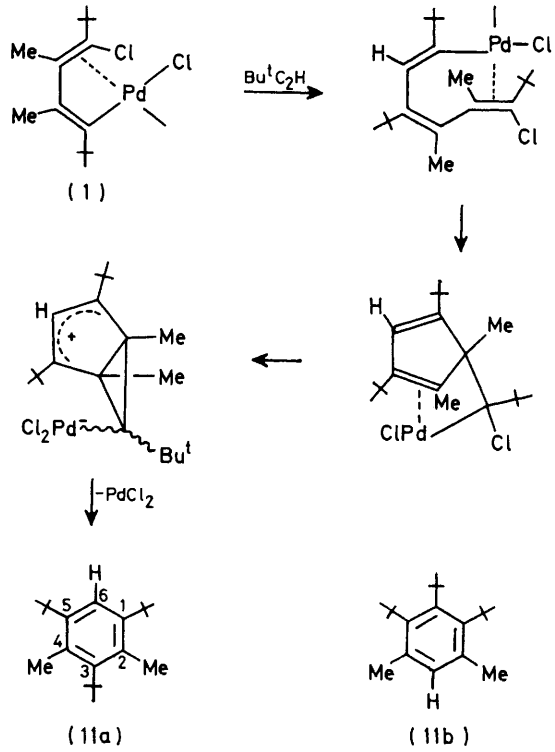
(10)

cyclopentadienone (10) was identified spectroscopically and by analogy with (4).

Reactions of σ-Butadienyl Complexes with 3,3-Dimethylbut-1-yne.—Although the insertion of a third bma into the Pd–C bond of complex (1) does not take place under ambient conditions [presumably because of the steric crowding about the metal and in particular because the t-butyl on C(3) would hinder the insertion of a large bma molecule into the Pd–C σ-bond],[1] our success in introducing CO into the molecule suggested that a smaller acetylene might react with (1).

When 3,3-dimethylbut-1-yne (mono-t-butylacetylene) was added to a toluene suspension of complex (1) reaction immediately occurred to give, in high yield, an organic compound which was shown to be a dimethyltri-t-butylbenzene. Both the ^1H and the ^{13}C n.m.r. spectra showed the two methyls and two of the t-butyl groups to be equivalent and this observation reduces the number of possible isomers to two, (11a) and (11b). Of these we rule out (11b) as improbable, (*i*) because the molecular rearrangements needed to generate (11b) in high yield from the butadienyl skeleton known to exist in (1) [1] are most unlikely, and (*ii*) because a benzene with three t-butyl groups adjacent would be extremely crowded and would be unlikely to be a particularly stable end-product. The formation of the benzene (11a) from (1) can be readily understood in terms of the cyclotrimerisation mechanism which one of us has previously advanced (Scheme 4).[14]

Further Reactions of Bipyridyl(σ-butadienyl)palladium Complexes (2) *and* (3).—Both the bipyridyl complexes (2) and (3) reacted with $[Pd(NCPh)_2Cl_2]$ to give $[Pd(bipy)Cl_2]$ and, initially, the σ,π-butadienyl complex (12),[1] which rapidly rearranged to give the cyclobutadiene complex (13).

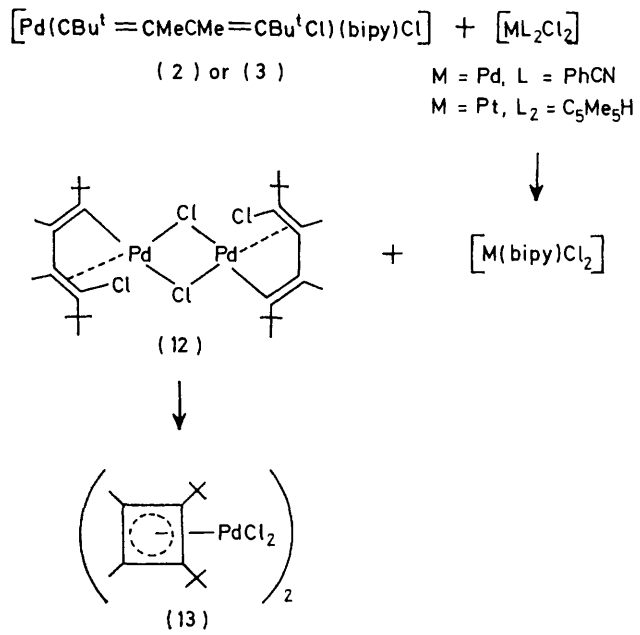


(1) (11a) (11b)

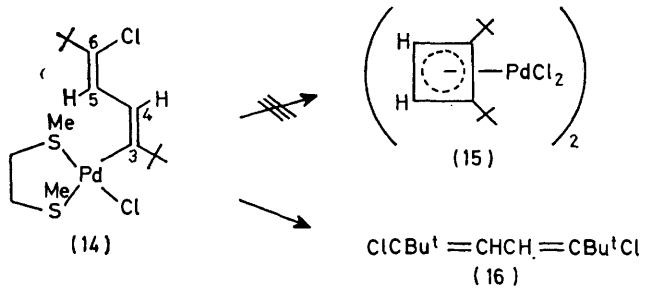
SCHEME 4

Two modes of reaction are possible in that either the σ,π-butadienyl or the bipyridyl ligand can be transferred from one Pd to the other. In order to distinguish between these alternatives the complex (3) was treated with a suitable soluble platinum(II) complex $[Pt(C_5Me_5H)Cl_2]$.[15] If the butadienyl ligand is being transferred, a cyclobutadieneplatinum complex would be formed, but if the bipy is transferred the complex (12) [or (13)] together with $[Pt(bipy)Cl_2]$ would be expected. The product of the reaction of (3) and $[Pt(C_5Me_5H)Cl_2]$ was complex (13) and $[Pt(bipy)Cl_2]$ and this showed that

the bipyridyl was the more labile ligand. This accords very well with our observations that bipy is readily lost from these complexes on carbonylation described above.



Since we now had a convenient method for removing the co-ligand from σ-butadienylpalladium complexes, we tried the analogous reaction with complex (14) [16] to see whether we could generate the hitherto unknown di-t-butylcyclobutadienepalladium complex (15). The reaction gave not the cyclobutadiene (15) but the organic 1,4-dichlorobutadiene (16) together with metal. This product is also obtained from higher-temperature reactions of $[Pd(NCPh)_2Cl_2]$ and 3,3-dimethylbut-1-yne.[17] Clearly, the intermediate, $[\{Pd(CBu^t{=}CHCH{=}CBu^t)Cl\}_n]$, has little tendency to cyclise and reductively eliminates (16) and Pd instead. This result again points to the importance of steric factors in determining the mode of reaction; without the bulky methyls at C(4) and C(5) of the butadienyl in (14) the *s-trans* conformation is preferred for the C(4)–C(5) bond and there is no driving force for the cyclisation.



EXPERIMENTAL

All reactions were carried out under nitrogen. N.m.r. spectra were recorded on Perkin-Elmer R-12B (60 MHz) and Varian HA-100 (100 MHz) (for ^1H) and JEOL PFT-100 (^{13}C) spectrometers using tetramethylsilane as internal reference. Far-i.r. spectra were recorded (as Nujol mulls) on a Perkin-Elmer PE-180 spectrometer. Microanalyses were determined by Sheffield University Microanalytical Service.

Reaction of [Pd(CBu^t=CMeCMe=CBu^{t}Cl)(bipy)Cl] (3) *with Carbon Monoxide.*—Carbon monoxide was passed through a filtered solution of complex (3) (0.53 g, 1 mmol) in moist benzene (15 cm^3) at 20 °C; after 5 min a small amount of 2,2′-bipyridyldichloropalladium was formed. The carbon monoxide was passed for another 10 min and the orange solution obtained was evaporated under reduced pressure. The residual yellow solid was extracted with pentane (20 cm^3) and the solution was chromatographed on silica gel in pentane. Evaporation of the orange-red band gave 3,4-dimethyl-2,5-di-t-butylcyclopentadienone (4) as orange-red needles (yield 32 mg, 10%, m.p. 32 °C) [Found: C, 80.7; H, 10.1%; *M* (mass spectroscopic) 220. $C_{15}H_{24}O$ requires C, 81.7; H, 10.9%; *M* 220]. ^1H N.m.r. (C^2HCl_3): δ 1.18 (Bu^t) and 1.99 (Me) p.p.m. ^{13}C N.m.r. (C^2HCl_3): δ 13.2 (Me), 30.7 (CMe_3), 33.1 (CMe_3), 130.7 [C(3)], 148.8 [C(2)], and 203.9 p.p.m. (CO). I.r.: ν(CO) at 1 710vs cm^{-1}. Starting material (0.32 g) was recovered unchanged.

Reaction of [Pd(CBu^t=CMeCMe=CBu^{t}Cl)(bipy)Cl] (2) *with Carbon Monoxide.*—Carbon monoxide was passed through a stirred solution of complex (2) (0.53 g, 1 mmol) in dichloromethane (20 cm^3) at 20 °C. After 10 min a pale yellow precipitate of complex (6) was formed. This was filtered off, washed with diethyl ether, and dried in air (yield 0.31 g, 72%) [Found: C, 46.1; H, 6.0; Cl, 17.4. $(C_{15}H_{24}Cl_2OPd)_n$ requires C, 45.4; H, 6.0; Cl, 17.8%]. ^1H N.m.r. (C_5H_5N): δ 1.07, 1.46 (2 × Bu^t), 1.55, and 2.42 p.p.m. (2 × Me). I.r.: ν(CO) at 1 710vs cm^{-1}, ν(Pd–Cl) at 225m, 260m, and 278s cm^{-1}.

Reaction of Complex (6) *with Pyridine.*—(*i*) *To give complex* (7). Pyridine (80 mg, 1 mmol) was added to a suspension of complex (6) (0.39 g, 1.0 mmol) in dichloromethane (20 cm^3) and the mixture stirred for 18 h to give a pale yellow solution. This was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was washed with pentane and crystallised from dichloromethane and light petroleum (b.p. 60—80 °C) to give pale yellow crystals of complex (7) (yield 0.21 g, 54%) [Found: C, 50.1; H, 6.6; Cl, 9.9%; *M* (osmometric in $CHCl_3$) 722. $C_{30}H_{22}Cl_2O_2Pd_2$ requires C, 49.9; H, 6.4; Cl, 9.8%; *M* 720]. ^1H N.m.r. (CH_2Cl_2): δ 1.24, 1.27 (2 × Bu^t), 2.05 (Me), 4.05, 4.20 p.p.m. [2 × d, *J*(H–H) = 2.4 Hz, CH_2]. I.r.: ν(CO) at 1 705vs cm^{-1}, ν(Pd–Cl) at 254s and 260s cm^{-1}.

(*ii*) *To give complex* (8). Pyridine (0.5 ml, 5 mmol) was added to a suspension of complex (6) (0.39 g, 1.0 mmol) in dichloromethane (20 cm^3) and the mixture stirred for 0.25 h at 20 °C, to give a yellow-orange solution. This was reduced in volume, light petroleum (20 cm^3) added, and the solution was left to crystallise at 20 °C. Orange crystals of complex (8) were formed which were filtered off and washed with light petroleum (yield 0.31 g, 69%) [Found: C, 54.0; H, 6.4; N, 2.7%; *M* (osmometric in $CHCl_3$) 398. $C_{20}H_{28}ClNOPd$ requires C, 54.5; H, 6.4; N, 3.2%; *M* 403]. ^1H N.m.r.: (CH_2Cl_2) δ 1.0, 1.33 (2 × Bu^t), 2.14 (Me), 4.20, 4.29 p.p.m. [2 × d, *J*(H–H) = 2.4 Hz, CH_2]; (pyridine) δ 1.29, 1.32 (2 × Bu^t), 2.08 (Me), 4.34, 4.47 p.p.m. [2 × d, *J*(H–H) = 2.4 Hz, CH_2]. ^{13}C N.m.r. (C^2HCl_3): δ 13.2 (Me), 29.7, 30.1 (2 × CMe_3), 34.3, 36.2 (2 × CMe_3), 59.9 (CH_2), 93.9 [C(1)], 124.5 [C(2)], 141.6 [C(3)], 150.7 [C(4)], 202.8 [C=O], 125.2, and 138.8 p.p.m. (py). I.r.: ν(CO) at 1 700vs cm^{-1}, ν(Pd–Cl) at 280s cm^{-1}.

Reactions of Acetylenes and Carbon Monoxide to give Cyclopentadienones.—(*i*) 3,4-*Dimethyl*-2,5-*di*-t-*butylcyclopentadienone* (4). A solution of 4,4-dimethylpent-2-yne (0.48 g, 10 mmol) in chlorobenzene (5 cm^3) was added over 10 min to a refluxing chlorobenzene solution of bis(benzonitrile)-dichloropalladium (38 mg, 0.1 mmol) containing benzonitrile (100 μl, 1 mmol), through which a steady stream of carbon monoxide was being passed. Carbon monoxide was then passed through the solution for another 10 min, the resulting deep red solution was allowed to cool, filtered, evaporated (to 5 cm^3), and pentane (20 cm^3) was added. Evaporation of the pentane solution under reduced pressure gave orange-red needles of the dimethyldi-t-butylcyclopentadienone (4) (0.18 g, m.p. 32 °C). The yellow solid remaining after the pentane extraction was crystallised from dichloromethane and pentane to yield complex (7) (yield 24 mg, based on Pd). The yield of (4) represents a turnover of 8.1 molecules of cyclopentadienone per palladium.

(*ii*) *Tetraphenylcyclopentadienone.* Diphenylacetylene (1.0 g) was allowed to react under the conditions described above; this gave a purple solution which, after chromatography on Florisil, gave purple tetraphenylcyclopentadienone (0.28 g, turnover eight molecules per Pd), and some hexaphenylbenzene, identified by comparison with authentic specimens.

(*iii*) 3,4-*Diphenyl*-2,5-*di*-t-*butylcyclopentadienone.* t-Butyl(phenyl)acetylene (1.0 g) was allowed to react under the conditions described above; this gave a red solution which, after chromatography on silica, gave orange needles of 3,4-diphenyl-2,5-di-t-butylcyclopentadienone (0.12 g, turnover three molecules per Pd) [Found: C, 87.1; H, 8.1%; *M* (mass spectroscopic) 344. $C_{25}H_{28}O$ requires C, 87.2; H, 8.2%; *M* 344]. ^1H N.m.r. (C^2HCl_3): δ 1.08 (s, 2 × Bu^t) and 7.0 p.p.m. (m, 2 × Ph). ^{13}C N.m.r. (C^2HCl_3): δ 31.0 (CMe_3), 33.1 (CMe_3), 132.0 [C(3)], 153.5 [C(2)], 204.2 (*C*=O), 126.7, 127.0, 129.5, 136.3 p.p.m. (Ph). I.r.: ν(CO) at 1 712vs cm^{-1} (in hexane solution).

Reaction of Complex (1) *with* 3,3-*Dimethylbut*-1-*yne to give* 1,3-*Dimethyl*-2,4,6-*tri*-t-*butylbenzene.*— 3,3-Dimethylbut-1-yne (0.4 g, 4.5 mmol) was added to a stirred suspension of freshly prepared complex (1) (0.55 g, 0.5 mmol) in toluene (20 cm^3). After 0.5 min the suspension dissolved to give a dark yellow solution which was evaporated to dryness under reduced pressure and extracted with pentane. The pentane solution was chromatographed on alumina in pentane, to give a colourless eluate which was evaporated to dryness under reduced pressure to give 1,3-dimethyl-2,4,6-tri-t-butylbenzene (11a) as a white solid. This was purified by crystallisation from hot ethanol to give colourless crystals (yield 0.27 g, 78%) [Found: C, 86.8; H, 12.8%; *M* (mass spectroscopic) 274. $C_{20}H_{34}$ requires C, 87.5; H, 12.4%; *M* 274]. ^1H N.m.r. (C^2HCl_3): δ 7.31 (s, H), 2.49 (s, 2 × Me), 1.53 (s, Bu^t), and 1.41 p.p.m. (s, 2 × Bu^t). ^{13}C N.m.r. (C^2HCl_3): δ 23.9 (2 × Me), 33.3, 31.9 (2 × CMe_3), 39.0, 36.6 (2:× CMe_3), 121.8 (*C*–H), 134.5 [C(2), C(4)], 144.6 [C(3), C(5)], and 151.1 p.p.m. [C(1)].

Reaction of Complex (2) *with* $[Pd(NCPh)_2Cl_2]$ *to give the Cyclobutadiene Complex* (13).—A solution of $[Pd(NCPh)_2Cl_2]$ (0.38 g, 1 mmol) in dichloromethane (10 cm^3) was added with stirring to a solution of complex (2) (0.52 g, 1 mmol) in dichloromethane (10 cm^3). A yellow precipitate of $[Pd(bipy)Cl_2]$ was formed and was filtered off. The yellow solution was evaporated under reduced pressure and the residual solid was washed with light petroleum and dried in air. The ^1H n.m.r. spectrum of the yellow solid in dichloromethane was recorded and the product identified as $[\{Pd(CBu^t{=}CMeCMe{=}CBu^tCl)Cl\}_2]$ (12); after standing for 0.5 h the spectrum had changed to that of the cyclobutadiene complex $[\{Pd(C_4Bu^t_2Me_2)Cl_2\}_2]$ (13). Complex (3) underwent an identical reaction.

Reaction of Complex (3) *with* $[Pt(C_5Me_5H)Cl_2]$ *to give the Cyclobutadiene Complex* (13).—A solution of complex (3) (0.26 g, 0.5 mmol) in chloroform was warmed to 50 °C with $[Pt(C_5Me_5H)Cl_2]$ (0.21 g, 0.5 mmol). A yellow precipitate of 2,2′-bipyridyldichloroplatinum was formed slowly; after 15 h the precipitate was filtered off and the filtrate was evaporated under reduced pressure. The residue was extracted with pentane which, on evaporation, left an oil shown to contain C_5Me_5H by ^1H n.m.r. spectroscopy. The yellow solid remaining was shown to be (13) by ^1H n.m.r. spectroscopy and analysis.[2]

Reaction of $[Pd(CBu^t{=}CHCH{=}CBu^tCl)\{MeS(CH_2)_2SMe\}Cl]$ (14) *with* $[Pd(NCPh)_2Cl_2]$.—Bis(benzonitrile)dichloropalladium (0.38 g, 1 mmol) in dichloromethane (10 cm^3) was stirred with a solution of (14) (0.47 g, 1 mmol) in dichloromethane (10 cm^3) at 20 °C. A black precipitate was formed which was filtered off; the filtrate was evaporated to dryness and extracted with pentane; on evaporation of the solvent from the extract an oil was obtained. The organic product was identified as $ClBu^tC{=}CHCH{=}CBu^tCl$ by ^1H n.m.r. and mass spectrometry [δ 1.21 (s, Bu^t) and 6.59 p.p.m. (s, CH); parent ion at *m/e* 235].

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