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# RECOLLECTIONS OF CYCLOMETALLATIONS AND CYCLIC ACETYLENES

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## Cyclometallated complexes

Chelate complexes of the transition elements in which one of the donors is a $\sigma$-bonded carbon atom, i.e. cyclometallated complexes, are commonplace nowadays and several reviews have appeared [1–5]. When I arrived at University College London in late 1960 to work as a Turner and Newall Fellow with the late Professor Ron Nyholm, cyclometallation was unheard of, metal–metal bonds existed mainly in dinuclear metal carbonyls, and terms such as oxidative addition and homogeneous catalysis by metal complexes were only just about to become popular. At University College, Nyholm was trying to extend his classic work on the coordination chemistry of *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(AsMe_2)_2$, to tertiary arsines containing an olefinic double bond suitably placed for chelation. A postdoctoral fellow, H.W. Kouwenhoven, who had left by the time I came, had made the first chelating mono-olefin complexes, $PtX_2$(ligand) (X = Cl, Br, I), derived from pent-4-enyldimethylarsine, $CH_2{=}CH[CH_2]_3AsMe_2$ [6], and two Ph.D. students, Ron Long and Gordon Erskine, were studying the platinum(II) complexes of (2-vinylphenyl)dimethylarsine, *o*-$CH_2{=}CHC_6H_4AsMe_2$, and (2-allylphenyl)dimethylarsine, *o*-$CH_2{=}CHCH_2C_6H_4AsMe_2$. The main interest centred on the complexes of formula *trans*-$PtBr_2(\text{ligand})_2$, in which only the arsenic atoms are coordinated. Nyholm's idea was that, although the double bonds were formally uncoordinated, they might nevertheless be able to interact with both the filled $d_{z^2}$ orbital or with the vacant $p_z$ orbital of platinum(II), and that this might affect their reactivity towards electrophiles and nucleophiles.

Some evidence for this notion had already been obtained. Long had studied the bromination of the complexes $PtBr_2(\text{ligand})_2$ formed by the isomeric 2-, 3-, and 4-(vinylphenyl)dimethylarsines. In all three cases three equivalents of bromine could be added. In the case of the complexes of the 3- and 4-isomers, the first equivalent of bromine clearly added to the metal to give red tetrabromoplatinum(IV) complexes $PtBr_4(Me_2AsC_6H_4CH{=}CH_2)_2$ (I and II), as expected, and the second and third equivalents added to the double bonds. However, in the case of $PtBr_2$(*o*-$Me_2AsC_6H_4CH{=}CH_2)_2$, the first equivalent of bromine appeared to add to one of the double bonds to give an orange-yellow compound formulated as a platinum(II) complex $PtBr_2(Me_2AsC_6H_4CHBrCH_2Br)(Me_2AsC_6H_4CH{=}CH_2)$ (III).

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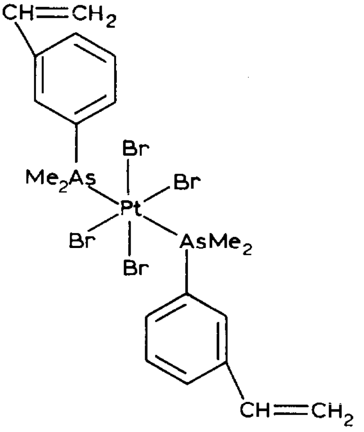
Erskine showed that a similar reaction sequence occurred for the complexes of the isomeric allylphenyldimethylarsines and discovered also that one of the bromine atoms in the supposed platinum(II) complex III, and in its analogue derived from (2-allylphenyl)dimethylarsine, was readily replaced on heating in methanol or ethanol to give an alkoxy derivative.

The clue to the correct interpretation of these intriguing results came from a conversation with Professor Chatt, who suggested that compound III was not a planar platinum(II) complex at all, but an octahedral platinum(IV) complex containing a metal–carbon σ-bond. I was at first reluctant to believe that such a compound could be generated by a reagent such as bromine, which usually cleaves metal–carbon σ-bonds. However, we were soon able to show, by independent synthesis, that structure III could not be correct [7], and an X-ray analysis of the mono-ethoxy derivative IV by Professor Ron Mason and Tony Towl at the University of Sheffield confirmed the essential correctness of Chatt's proposal [8,9] *. The structure con-



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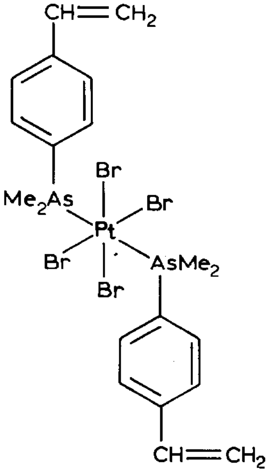

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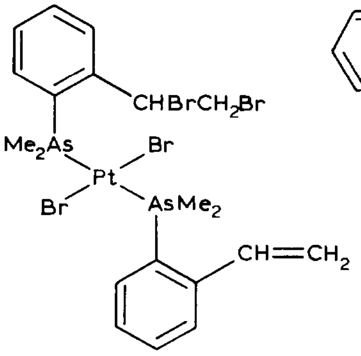

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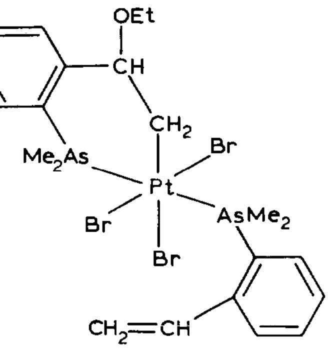

(IV)

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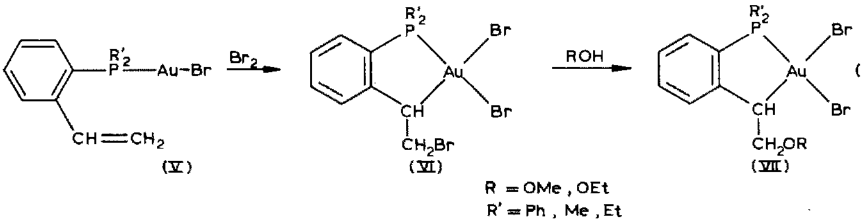
* Owing to an unfortunate mix-up of crystalline samples, this structure was initially reported [8] as being that derived from (2-allylphenyl)dimethylarsine.

tains a six-membered cyclometallated ring and the ethoxy group resides on the carbon *β* to platinum. Incidentally, this provided an early example of the ease of substitution of a halogen atom attached to a carbon which is *α* or *β* to a transition metal atom.

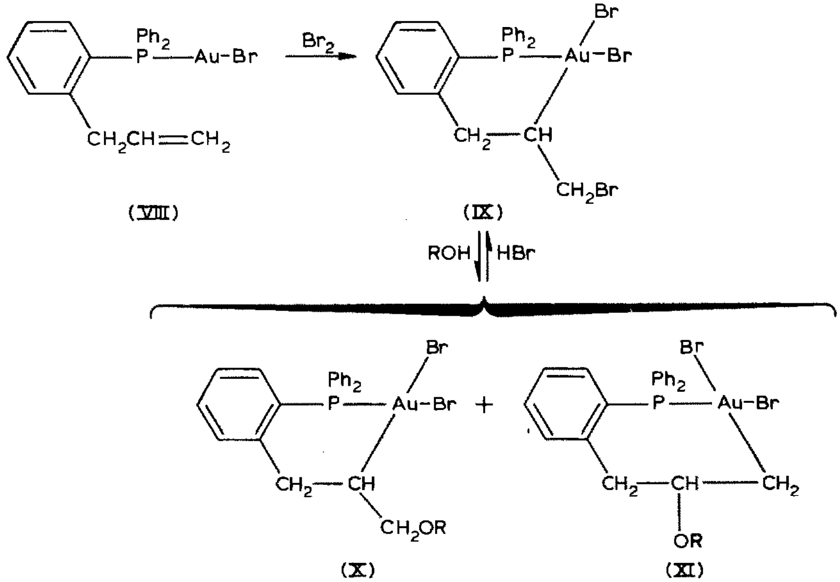
The $^1H$ NMR spectra of these platinum complexes were complex and we looked for other simpler systems which might show similar behaviour. A Ph.D. student, Bill Kneen, synthesized the bromogold(I) complex (V) of (2-vinylphenyl)diphenylphosphine, $o\text{-}CH_2{=}CHC_6H_4PPh_2$ and showed that it underwent a similar sequence of reactions on treatment with bromine and heating of the resulting gold(III) complex VI (R′ = Ph) with alcohols [10] (eq. 1).



(1)

The $^1H$ NMR spectrum of VI (R′ = Ph) suggested, and the X-ray structure confirmed, that this planar gold(III) complex, in contrast to the platinum(IV) complex IV, had a five-membered cyclometallated ring. Unfortunately, we were unable to grow good crystals of the alkoxy derivatives and, because their $^1H$ NMR spectra closely resembled that of IV, it seemed reasonable to assume that they must have a six-membered ring like that in IV. This implied, of course, that the chelate ring had expanded in the alcoholysis step, and we published the results in a preliminary communication with that interpretation [10].

Our recent X-ray and NMR ($^1H$, $^{13}C$, $^{31}P$) studies in Canberra [11], both on Kneen's original system and on the corresponding bromogold(I) complexes of (2-vinylphenyl)dimethylphosphine and (2-vinylphenyl)diethylphosphine (eq. 1; R′ =

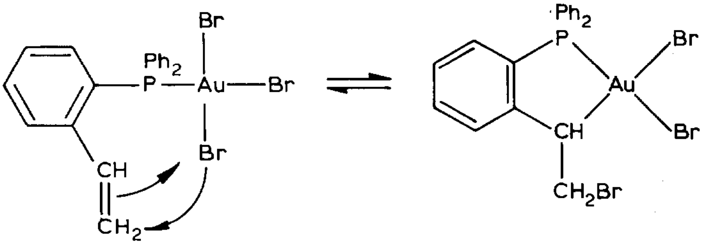


(2)

Me, Et) have shown beyond doubt that, for all three series, the initial product of bromination (VI) and the alcoholysis products (VII) contain five-membered cyclometallated rings as shown, and that no chelate ring expansion has occurred in these systems. Nevertheless, it does take place in the closely related gold complexes derived from (2-allylphenyl)diphenylphosphine, *o*-$CH_2$=$CHCH_2C_6H_4PPh_2$ [11] (eq. 2).

Treatment of AuBr(*o*-$Ph_2PC_6H_4CH_2CH$=$CH_2$) (VIII) with bromine gives a planar gold(III) complex (IX) containing a six-membered cyclometallated ring and, as Kneen had already observed at University College, this affords on heating with methanol or ethanol an approximately 1/1 mixture of alkoxy derivatives X and XI, which can be separated by fractional crystallization and chromatography. According to a recent X-ray study [11], X (R = OMe) is structurally similar to IX, but XI unexpectedly contains a seven-membered ring in which gold is now bound to the terminal carbon atom and the methoxyl substituent has moved to the 2-carbon atom. Interestingly, both X and XI react with HBr to regenerate IX as the sole product, demonstrating how easily the different size rings can interconvert and excluding any simple carbonium ion mechanism for the transformations.

This work started at University College London in the late fifties and has continued, on and off, till the present, yet there remain important unanswered questions. We still do not know the precise structure of Long's original compound III, although we do know that its ethoxy derivative has structure IV. The $^1H$ NMR spectrum of III suggests that, in solution, it may be a mixture of a cyclometallated complex (or complexes) of unknown ring size and a conventional tetrabromo complex $PtBr_4$(*o*-$Me_2AsC_6H_4CH$=$CH_2$)$_2$. Why are five-membered cyclometallated rings apparently favoured for planar gold(III) and platinum(II) [12], whereas a six-membered ring is formed preferentially for octahedral platinum(IV)? How does bromine add to the platinum(II) and gold(I) complexes and what is the mechanism of substitution of bromine by alkoxyl on the carbon atom in the cyclometallated rings? We have evidence that in the first step bromine adds to the metal atom to give a tribromogold(III) or tetrabromoplatinum(IV) intermediate such as XII and that a bromine atom then migrates reversibly to a carbon atom in the side-chain [13] (eq. 3). I suspect that the same intermediate, formed by the reverse migration of bromine from carbon to metal, is involved in the alcoholysis reactions. It contains an olefinic ligand attached to a metal in a high oxidation state and the double bond would be expected to be sensitive to nucleophilic attack.

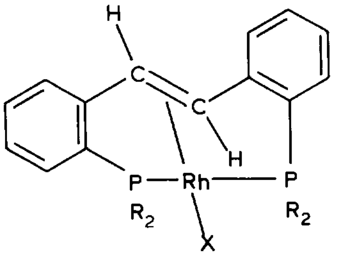


(XII) (XI)

(3)

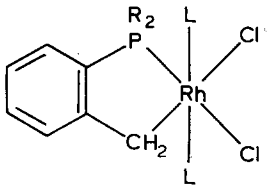
The work described above provided my first experience of cyclometallation, but while I was still at University College London two other Ph.D. students, Peter Longstaff and David Milner, had made closely related discoveries. Longstaff was working on the sterically bulky ligand tri-*o*-tolylphosphine, $P(o\text{-MeC}_6H_4)_3$, which, we thought, might stabilize a three-coordinate complex of rhodium(I), $RhClL_2$, and thus could model the species proposed as an intermediate in the reactions of $RhCl(PPh_3)_3$. Indeed, from the reaction of rhodium trichloride with tri-*o*-tolylphosphine in high-boiling solvents, Longstaff isolated a yellow, diamagnetic compound having the expected empirical formula, $RhCl\{P(o\text{-tolyl})_3\}_2$. Unfortunately, this compound was insufficiently soluble in organic solvents for its $^1H$ NMR spectrum or molecular weight to be measured, and its IR spectrum contained a mysterious, intense band at ca. 920 $cm^{-1}$ which was not present in the spectrum of tri-*o*-tolylphosphine itself. Longstaff suggested that the thiocyanate derivative might be more soluble, but I thought it unlikely, knowing how easily thiocyanate groups bridge between metal atoms. Fortunately, Longstaff ignored his supervisor's advice and made the nicely soluble thiocyanate derivative, the $^1H$ NMR spectrum of which provided the answer: the ratio of aromatic to methyl protons was 12/6 instead of 8/6 and there was a two proton doublet of triplets at $\delta$ 3.50 ppm. Clearly we had lost a pair of *o*-tolyl methyl groups and it did not take long to realise that we had generated a complex XIII containing a new chelating *trans*-stilbene ligand by dehydrogenative coupling of two *o*-tolylphosphine residues on rhodium [14]. The ligand itself could be displaced from rhodium by means of cyanide and its IR spectrum now had a band at 970 $cm^{-1}$, typical of an olefinic CH deformation mode in a *trans*-disubstituted olefin.

Longstaff also showed that, under milder conditions, the reaction of ethanolic $RhCl_3$ with tri-*o*-tolylphosphine gave a remarkable, blue, paramagnetic rhodium(II) complex, $RhCl_2\{P(o\text{-tolyl})_3\}_2$, and a colourless compound of apparent formula $RhCl_2\{P(o\text{-tolyl})_3\}$. The latter turned out to be another cyclometallated complex and from it, by the action of various ligands, Longstaff made a series of octahedral rhodium(III) complexes of the general type XIV containing the five-membered ring $\overline{\text{Rh-}o\text{-CH}_2\text{C}_6\text{H}_4\text{P}}(o\text{-MeC}_6\text{H}_4)_2$ [14]. These studies were, I believe, among the first to demonstrate the tendency of a bulky tertiary phosphine to promote cyclometallation at a transition metal centre [15].



XIII

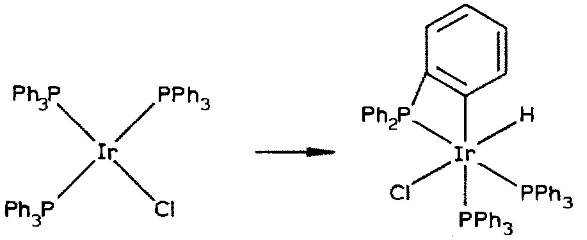
$R = o\text{—MeC}_6H_4$ ; $X = Cl$ , NCS



(XIV)

$R = o\text{ —MeC}_6H_4$

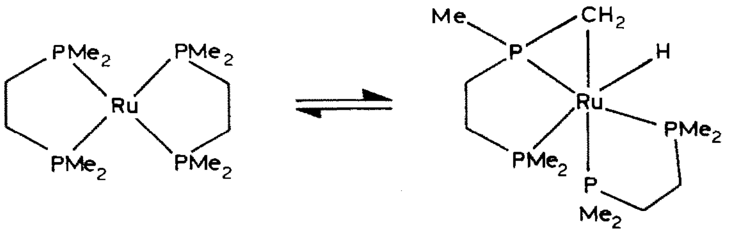
At about the same time, David Milner, taking time off from ICI to do a Ph.D., had been trying to make $IrCl(PPh_3)_3$, which we thought naively would be more reactive towards the oxidative addition of simple molecules than $RhCl(PPh_3)_3$. We knew that it could not be made analogously to $RhCl(PPh_3)_3$ simply by heating $IrCl_3$ with an excess of $PPh_3$ in ethanol, because Vaska [16] had already shown that this reaction gives hydridoiridium(III) complexes. Milner found that displacement of the olefins cycloocta-1,5-diene or, better, cyclooctene from their iridium(I) complexes $[IrCl(1,5\text{-}C_8H_{12})]_2$ or $[IrCl(C_8H_{14})_2]_2$ at room temperature in hexane precipitated $IrCl(PPh_3)_3$ as an orange, air-sensitive, microcrystalline solid. To our surprise, when solutions of the compound in various organic solvents were set aside or warmed, the colour faded and a white solid of the same composition was formed which had a typical $\nu$(Ir–H) band at 2200 $cm^{-1}$ in its IR spectrum. It took several months before we realised that the compound was not reacting with the solvents and that we had an example of an internal oxidative addition in which a hydrogen atom migrates from an *ortho*-position in one of the triphenylphosphine ligands to the metal [17] (eq. 4).



(XV) (XVI)

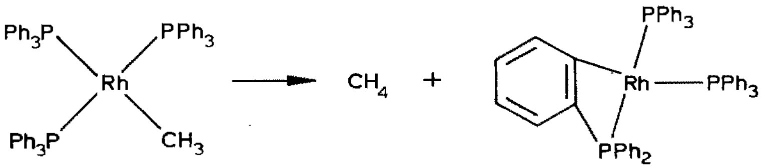
(4)

At the time, the closest analogy we could find for this behaviour was the tautomeric equilibrium between ruthenium(0) and ruthenium(II) studied by Chatt and Davidson [18] (eq. 5), although in this case it does not seem to be possible to isolate the low-valent metal tautomer as a discrete species.



(5)

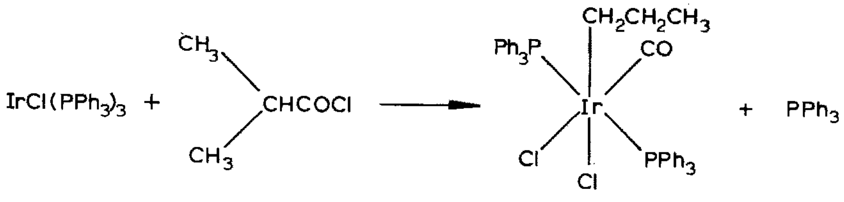
Shortly after we had published our preliminary communication [18], Ron Nyholm passed on to me a pre-print from George Parshall at Dupont in which was reported the remarkable observation that nineteen hydrogen atoms in the dinitrogen complex $CoH(N_2)(PPh_3)_3$ exchange with $D_2$ [19]; *ortho*-metallated intermediates were proposed. I also learnt later from Willi Keim of his initial puzzlement over the observation made at Shell-Emeryville that $Rh(CH_3)(PPh_3)_3$ decomposes on heating to give 1 mol of methane per mol of complex and the subsequent realisation that this too is an *ortho*-metallation process [20] (eq. 5).



(5)

In 1967 I moved to the newly established Research School of Chemistry at the A.N.U., where David Milner completed his Ph.D. work on the *ortho*-metallation of

$IrCl(PPh_3)_3$. I continued to study the chemistry of the various chelating olefinic ligands which we had started at University College and, with postdoctoral fellows Bob Watt, Barry Tomkins, Bob Johnson, and Peter Clark, and a Ph.D. student, Jim Hann, uncovered a variety of cyclometallations, coupling reactions, and sometimes both, on metals such as rhodium, iridium, ruthenium, nickel, palladium, and platinum [21]. Another Ph.D. student, Romeo Charles, followed up Milner's work and discovered the unexpected secondary to normal alkyl group rearrangement that occurs during the oxidative addition of α-branched acyl halides to $IrCl(PPh_3)_3$ [24], an example of which is shown in eq. 6.

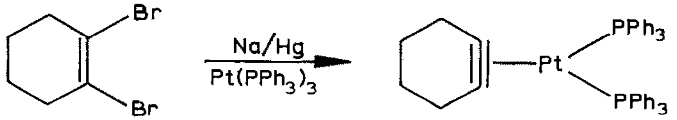


(6)

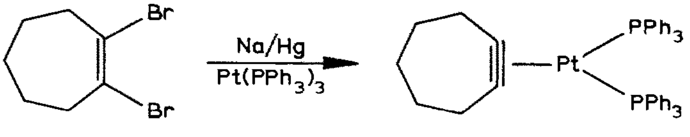
## Cyclic acetylene complexes

The move to Canberra gave me the opportunity to branch out into other areas. I was especially impressed by Pettit's elegant work on the stabilization of cyclobutadiene via its $Fe(CO)_3$ complex and on the generation of the transient hydrocarbon by oxidation of the complex [23]. I thought this approach might be capable of extension to small ring alkynes such as cyclohexyne, cycloheptyne, and benzyne, which exist only as transient intermediates in the free state [24,25]. The smallest simple cyclic alkyne that can be isolated is cyclooctyne, and even this compound is considerably more reactive than larger cyclic alkynes or acyclic alkynes. In small ring alkynes the bonds at the acetylenic carbon atoms cannot be collinear but must be bent back, and since this is what happens when alkynes form metal complexes, the complexes of small ring alkynes should be exceptionally stable. The idea was, therefore, to generate the short-lived alkynes in the presence of a suitable metal complex. The ideal compound for this purpose seemed to be $Pt(PPh_3)_3$, which was known to form stable alkyne complexes under mild conditions.

When Dr. Toshikatsu Yoshida arrived in my group from Osaka in 1970, I put the idea to him, somewhat hesitantly, as I was not too confident of success, knowing that the estimated half-life of cyclohexyne is only a few seconds at −110°C, while that of cycloheptyne is ca. 1 h at −5°C [26]. Within a few months, this most skilful



(6)

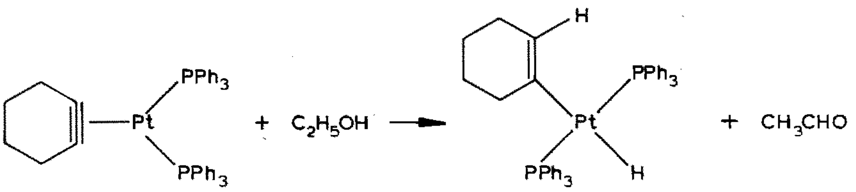


(7)

researcher had isolated the first platinum(0) complexes of these transient species in good yield (eq. 6 and 7) and their molecular structures had been determined by single crystal X-ray diffraction [27–29].

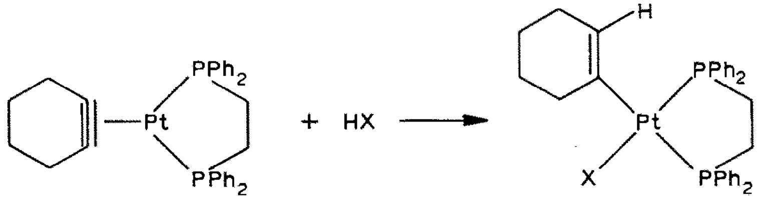
Despite the success of the experiment, it seems likely that the premise on which it was based is wrong, i.e. the complexes are not formed by generation of free cyclohexyne or cycloheptyne and subsequent trapping of these species with $Pt(PPh_3)_3$. Rather, the 1,2-dibromocycloalkenes form $Pt(PPh_3)_2$(olefin) complexes which are reduced by sodium amalgam to the cyclic alkyne derivatives [30]. Not surprisingly, the cyclic alkynes are not easily displaced from these complexes and, for example, the chelate ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) replaces only the triphenylphosphine ligands, leaving the cyclic alkynes intact. Despite this, the discovery of these compounds has opened up new areas of interest which were quite unforeseen when the original proposal was formulated.

In attempting to grow single crystals of the cyclohexyne complex $Pt(C_6H_8)(PPh_3)_2$ from benzene/ethanol, Yoshida discovered that the $\eta^1$-cyclohexenylhydridoplatinum(II) complex *trans*-$PtH(C_6H_9)(PPh_3)_2$ was formed [31] (eq. 8).



(8)

This reaction is just one example of a characteristic feature of the chemistry of cyclohexyneplatinum(0) complexes, namely, their ready protonation by a variety of weak acids [29,31] (eq. 9). Of particular interest are the reactions of $Pt(C_6H_8)$(dppe) with water and methanol, which generate monomeric, $\eta^1$-cyclohexenyl-hydroxo- and -methoxoplatinum(II) complexes, respectively. These compounds contain both "soft" and "hard" ligands together in the coordination sphere of a typical Class B metal ion, and their $^{31}P\{^1H\}$ NMR spectra provide useful information about the positions of carbon donor ligands in the *trans*-influence series [32]. Also remarkable is the thermal stability of the methoxo complex $Pt(OMe)(C_6H_9)$(dppe), because alkoxo-tertiary phosphine complexes of the later transition elements generally decompose so readily by $\beta$-hydride migration that they cannot be isolated. Indeed, an alkoxo complex is the presumed precursor to *trans*-$PtH(C_6H_9)(PPh_3)_2$ (eq. 8). These observations led Drs. Trevor Appleton and Dennis Arnold to synthesize a range of monomeric hydroxoplatinum(II) complexes containing either *trans*-monodentate

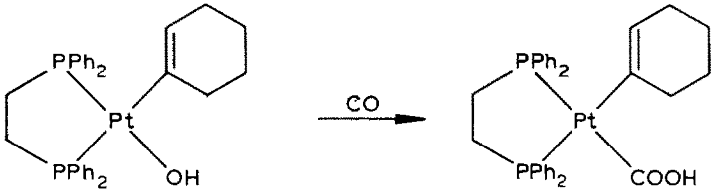


(9)

(HX = $H_2O$, $CH_3OH$, $p$-$MeC_6H_4OH$, PhSH, $CH_3CN$, $PhCH_2CN$, $PhCOCH_3$,
$CH_3NO_2$, $CH_3CONH_2$)

tertiary phosphines or a *cis*-bidentate ditertiary phosphine, and containing common $\sigma$-donor ligands such as methyl or phenyl in place of cyclohexenyl [32,33]. The complexes *trans*-$Pt(OH)R(PR'_3)_2$ are useful precursors to *trans*-hydrido(alkyls) and *trans*-hydrido(aryls) of platinum(II), $PtHR(PR'_3)_2$, which were not previously readily accessible [34].

In addition to their ability to catalyse homogeneously the hydration of nitriles to carboxamides [33,35], the hydroxoplatinum(II) complexes undergo other interesting reactions. Carbon monoxide inserts at room temperature into Pt–OH bonds to give



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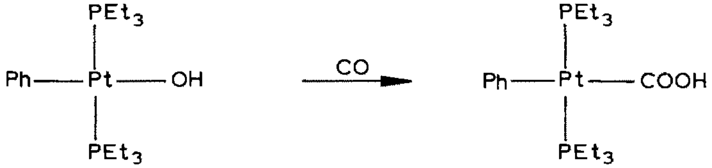
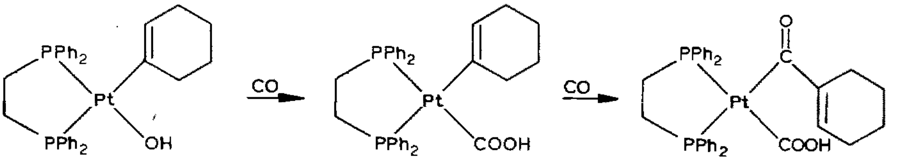


$$Ph-\overset{PEt_3}{\underset{PEt_3}{Pt}}-OH \xrightarrow{CO} Ph-\overset{PEt_3}{\underset{PEt_3}{Pt}}-COOH \qquad (11)$$

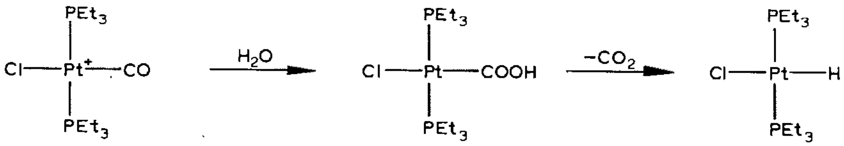
metallocarboxylic acids or metal hydroxycarbonyls of considerable thermal stability [36] (eq. 10, 11).

In the case of the corresponding complex $Pt(OH)(C_6H_9)\{Ph_2P(CH_2)_3PPh_2\}$ a second insertion into the Pt–$C_6H_9$ bond is also observed under ambient conditions [37] (eq. 12). The ability to promote CO insertion into Pt–C bonds seems to be characteristic of 1,3-bis(diphenylphosphino)propane, although it is not clear why it should be more effective than 1,2-bis(diphenylphosphino)ethane.



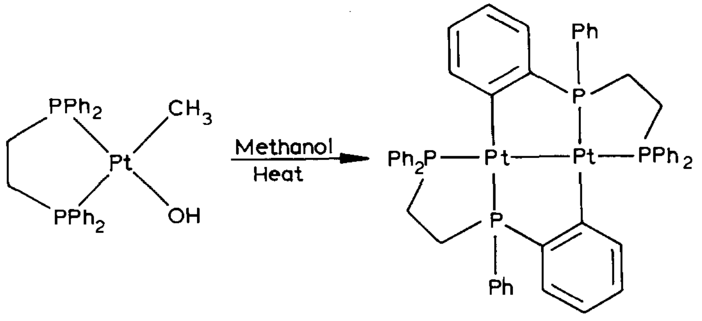
(12)

Metallocarboxylic acids of the transition elements are still fairly uncommon; in most cases, they appear to decompose readily by $\beta$-hydride migration and elimination of $CO_2$. An example is shown in eq. 13 [38]. This is not the case for our compounds, though their mode of decomposition has not yet been fully elucidated.



$$Cl-\overset{PEt_3}{\underset{PEt_3}{Pt^+}}-CO \xrightarrow{H_2O} Cl-\overset{PEt_3}{\underset{PEt_3}{Pt}}-COOH \xrightarrow{-CO_2} Cl-\overset{PEt_3}{\underset{PEt_3}{Pt}}-H \qquad (13)$$

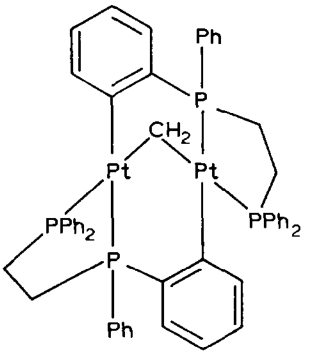
A second interesting reaction is that of $Pt(OH)(CH_3)(dppe)$ in refluxing methanol, which coincidentally provides a link with our earlier cyclometallation studies (eq. 14). The orange product of empirical formula $[Pt(dppe)]_2$ is a dinuclear platinum(I) complex XVII in which two $d^9$ metal atoms, 2.628 Å apart, are bridged by a pair of *ortho*-metallated dppe units [39]. The presence of the metal–carbon bonds in systems



(14)

(XVII)

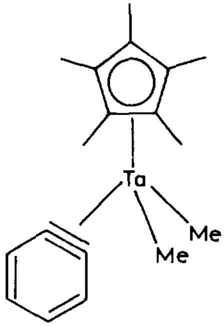
of this type should activate the metal centres to oxidative addition and various reactions which lead to novel A-frame dimers have been observed. For example, methyl iodide reacts with XVII to give a 1/1 adduct which is readily and reversibly deprotonated to the neutral μ-methylene complex XVIII [40].



(XVIII)

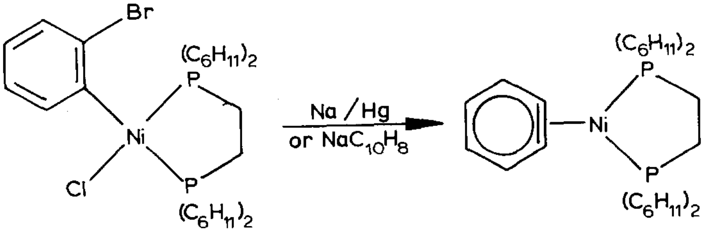
We are now looking for general syntheses of dinuclear complexes of the transition elements which contain bridging, cyclometallated arylphosphine and arylarsine ligands, and Dr. Bhargava has made the parent member of the series, $Au_2(C_6H_4PPh_2)_2$, by reaction of $AuBr(PEt_3)$ with $o$-$LiC_6H_4PPh_2$. Obviously this research has moved a long way from the original objective of studying cyclic alkyne complexes, although it stemmed directly from that work.

Recently we have returned to the problem of forming stable, mononuclear, transition metal complexes of benzyne (1,2-dehydrobenzene), $C_6H_4$. There have been several unsuccessful attempts to make mononuclear benzyne complexes of the $d^{10}$ elements, such as $Pt(C_6H_4)(PPh_3)_2$ [41–43] and $Ni(C_6H_4)(PEt_3)_2$ [44], and an early claim to have made a benzyne nickel carbonyl complex was later withdrawn [45]. There are several binuclear or trinuclear compounds that contain bridging $C_6H_4$ units, but the only structurally characterized mononuclear benzyne complex is Schrock's tantalum compound XIX, which was made by thermal decomposition of $Ta(\eta\text{-}C_5Me_5)(C_6H_5)Me_3$ [46].



(XIX)

After many months of tantalizing failure, Dr. Nick Roberts has isolated the first mononuclear benzyne complex of nickel(0) (XX), prepared in ca. 60% yield as shown in eq. 14 [47]. It is a yellow, crystalline solid which undoubtedly owes much of its stability to the presence of the bulky cyclohexyl groups on the ditertiary phosphine.



(XX)

(14)

The X-ray structure of the complex shows that the complexed ‘C≡C’ bond length is 1.322(6) Å cf. 1.364(5) Å in the tantalum compound XIX [46,48]. Both distances are significantly longer than those found in typical acyclic alkyne complexes of $d^{10}$ metals, or in $Pt(C_6H_8)(PPh_3)_2$ (1.25–1.30 Å); this is as expected, since benzyne itself is not a fully fledged alkyne. Interestingly, the remaining ring C–C distances in XX are equal, within experimental error, at 1.385 Å, whereas those in XIX show slight, but significant, alternation (1.367 ± 0.007 and 1.407 ± 0.007 Å). Perhaps this indicates that in the tantalum compound both orthogonal $\pi$-orbitals interact with the metal atom, whereas in the nickel compound only the in-plane $\pi$-orbitals do so. The $Ni-C_6H_4$ bond in XX undergoes insertion with unsaturated molecules such as $CO_2$, $C_2H_4$ and $MeO_2CC_2CO_2Me$ under mild conditions [47]. If complexes similar to XX containing sterically less demanding ligands can be made, they may prove to be synthetically useful precursors in organometallic and organic chemistry.

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