Regiospecific Hydride Abstraction from Metallacycles: Conversion of Metallacyclopentanes to Cationic π-Allylic Complexes †

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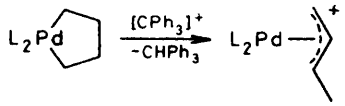
The rhoda- and irida-cyclopentane complexes [M(CH$_2$CH$_2$CH$_2$CH$_2$)(η^5-C$_5$Me$_5$)(PPh$_3$)] [M = Rh (1) or Ir (2)] react with the trityl cation [CPh$_3$]$^+$ to give the η^3-1-methylallyl derivatives [M(η^3-CH$_2$CHCHMe)(η^5-C$_5$Me$_5$)(PPh$_3$)][BF$_4$] [M = Rh (3) or Ir (4)]. Deuterium-labelling studies show that in these cases as well as in the previously reported palladacyclopentane → (η^3-1-methylallyl)palladium complex transformations, the trityl cation abstracts regiospecifically one of the β-hydrogen atoms of the metallacyclic moiety. The involvement of a σ-3-butenyl intermediate which rearranges to a η^3-1-methylallyl derivative is confirmed by reacting the palladium and rhodium dihalides, [PdCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] and [Rh(η^5-C$_5$Me$_5$)(PPh$_3$)I$_2$], with 3-butenylmagnesium bromide. In the case of palladium a σ-3-butenyl complex is obtained which, by reacting with AgBF$_4$, gives the η^3-1-methylallyl derivative [Pd(η^3-CH$_2$CHCHMe)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)][BF$_4$]. In the case of rhodium the PPh$_3$ ligand is lost and the η^3-1-methylallyl compound [Rh(η^3-CH$_2$CHCHMe)(η^5-C$_5$Me$_5$)I] is obtained directly. By reacting [Rh(η^5-C$_5$Me$_5$)(PPh$_3$)I$_2$] with 3-pentenylmagnesium bromide, the η^3-1,3-dimethylallyl complex [Rh(η^3-MeCHCHCHMe)(η^5-C$_5$Me$_5$)(PPh$_3$)][BF$_4$] is obtained. Mechanistic implications are discussed along with the significance of the reactions studied in connection with the role of transition-metal metallacyclopentane derivatives in organometallic chemistry and in catalysis.

Metallacycles, by virtue of their structure, exhibit a very versatile chemistry which resembles only in some features that of acyclic dialkyls.[1]

In the course of our studies on the preparation and reactivity of such compounds we found that palladacyclopentanes undergo a facile hydrogen abstraction by the trityl cation to give cationic π-allyl derivatives of palladium(II):[2] equation (i) [L$_2$ = neutral ligand(s)]. Because of the novelty



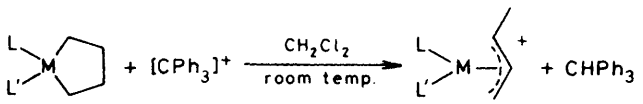
(i)

of this reaction which inter-relates two important classes of organometallics and the potential implication of a metallacyclopentane → π-allyl metal hydride transformation in transition-metal metallacycle chemistry,[1] we were induced to check the generality of this reaction and to investigate its mechanism.

In this paper, we report the results obtained by reacting the rhodium and iridium metallacyclopentane derivatives, (1) and (2), with [CPh$_3$]$^+$ to give π-butenyl compounds. We present also an account of our study of the mechanism of the reaction. As discussed later, three principal conclusions emerge from our data: (*a*) the trityl cation abstracts regiospecifically one of the β-hydrogen atoms of the metallacyclic ring; (*b*) a σ-3-butenyl cationic compound is probably involved as intermediate species; (*c*) σ-3-butenyl complexes of palladium and rhodium easily rearrange to η^3-1-methylallyl derivatives.

Results and Discussion

Reaction of Rhoda- and Irida-cyclopentanes with the Trityl Cation.—The metallacycles (1) and (2) react rapidly with [CPh$_3$]$^+$ in CH$_2$Cl$_2$ at room temperature to give solutions from



(1) M = Rh, L = η^5-C$_5$Me$_5$, L' = PPh$_3$ (3)
(2) M = Ir, L = η^5-C$_5$Me$_5$, L' = PPh$_3$ (4)
(5) M = Pd, L = L' = PPh$_3$ or L—L' = dppe or bipy (6)

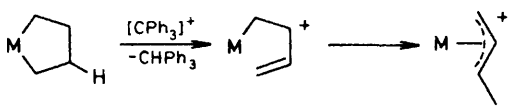
Scheme 1. dppe = 1,2-bis(diphenylphosphino)ethane, bipy = 2,2'-bipyridyl

which, by precipitation with diethyl ether, the tetrafluoroborate salts of the η^3-1-methylallyl cations (3) and (4) are recovered in high yields (Scheme 1).

The structural assignment is based mainly on the ^{1}H and ^{13}C n.m.r. spectra (Table), and, in the case of (3) is also confirmed by comparison with an authentic sample prepared by literature methods.[3]

These results together with the already reported conversion of the palladacyclopentanes (5) to the cationic η^3-1-methylallyl compounds (6) [2] (Scheme 1) provide a basis for looking at this reaction as a common feature for metallacyclopentane compounds.

As it was proposed in a previous paper,[2] the formation of η^3-1-methylallyl complexes could be easily explained assuming an initial β-hydride abstraction by the trityl cation followed by a rapid isomerization of the resulting 3-butenyl intermediate to the π-allyl complex: equation (ii). The first step is well



(ii)

documented in the literature for linear alkyls and has been used to convert iron alkyls into the corresponding π-bonded

† *Non-S.I. units employed:* eV = 1.602 × 10^{-19} J, mmHg = 133.3 Pa.

Table. Hydrogen-1 and carbon-13 n.m.r. data [a] for the complexes

Complex	^{1}H N.m.r.	^{13}C N.m.r.
(3) [Rh(η^3-$CH_2CHCHMe$)(η^5-C_5Me_5)(PPh_3)][BF_4]	1.50 [d, 15 H, C_5Me_5, J(PH) 3], 1.54 (d, 3 H, Me), 1.77 (m, 1 H, H_a), 2.44 (m, 1 H, H_b), 3.06 [d, 1 H, H_s, J(HH) 7], 3.94 (m, 1 H, H_c), 7.50 (m, 15 H, Ph) [b,c]	9.16 (C_5Me_5), 17.14 (CH*Me*), 52.66 (CH_2), 69.92 (*C*HMe), 90.70 (CH_2*C*HCHMe), 101.98 (C_5Me_5), 127.80—134.36 (Ph) [b]
(4) [Ir(η^3-$CH_2CHCHMe$)(η^5-C_5Me_5)(PPh_3)][BF_4]	1.54 (m, 3 H, Me), 1.57 [d, 15 H, C_5Me_5, J(PH) 2.1], 1.59 [br d, 1 H, H_a, J(HH) ~ 9], 2.23 (m, 1 H, H_b), 2.86 [d, 1 H, H_s, J(HH) 7], 3.67 (m, 1 H, H_c), 7.39 (m, 15 H, Ph) [b,c]	
(7) [Pd($CH_2CD_2CD_2CH_2$)(dppe)]	1.86 [d, 4 H, P–CH_2, J(PH) 18], 2.94 [dd, 4H, Pd–CH_2, J(PH) 6], 6.9—7.18 and 7.48—7.76 (m, 20 H, Ph) [d]	
(8) [Rh($CH_2CD_2CD_2CH_2$)(η^5-C_5Me_5)(PPh_3)]	1.48 [d, 15 H, C_5Me_5, J(PH) 2], 1.98 (m, 4 H, CH_2), 7.18—7.52 (m, 15 H, Ph) [d]	9.62 (C_5Me_5), 24.28 (CH_2), 98.09 (C_5Me_5), 127.12—135.86 (Ph) [d]
(9) [Rh($CD_2CH_2CH_2CD_2$)(η^5-C_5Me_5)(PPh_3)]	1.48 [d, 15 H, C_5Me_5, J(PH) 2], 1.38 (m, 4 H, CH_2), 7.18—7.52 (m, 15 H, Ph) [d]	9.66 (C_5Me_5), 34.21 (CH_2), 98.12 (C_5Me_5), 127.32—135.75 (Ph) [d]
(10) [Pd(η^3-$CH_2CDCDCH_2D$)(dppe)][BF_4]	1.62 (m, 2 H, CH_2D), 2.56 [d, 4 H, P–CH_2, J(PH) 22], 3.01 (m, 1 H, H_a), 4.50 (m, 1 H, H_s), 7.0—8.0 (m, 20 H, Ph) [b,c]	28.73 (P–CH_2), 66.16 (CH_2CD), 129—134 (Ph) [b]
(11) [Rh(η^3-$CH_2CDCDCH_2D$)(η^5-C_5Me_5)(PPh_3)][BF_4]	1.51 [d, 15 H, C_5Me_5, J(PH) 3], 1.58 (s, 2 H, CH_2D), 1.71 [d, 1 H, H_a, J(PH) 12], 3.11 (s, 1 H, H_s), 7.50 (m, 15 H, Ph) [b,c]	9.18 (C_5Me_5), 52.69 (CH_2CD), 101.96 (C_5Me_5), 127.89—134.62 (Ph) [b]
(12) [Rh(η^3-$CD_2CHCHCD_2H$)(η^5-C_5Me_5)(PPh_3)][BF_4]	1.51 [d, 15 H, C_5Me_5, J(PH) 3], 1.55 [d, 1 H, CD_2H, J(HH) 6.5], 2.45 (m, 1 H, H_b), 4.01 (m, 1 H, H_c), 7.45 (m, 15 H, Ph) [b,c]	9.28 (C_5Me_5), 69.23 ($CHCD_2H$), 90.83 (CD_2CHCH), 102.28 (C_5Me_5), 127.90—134.89 (Ph) [b]
(13) [Pd(σ-$CH_2CH_2CHCH_2$)Cl(dppe)]	1.85 [d, 4 H, P–CH_2, J(PH) 18], 2.1 (m, 2 H, Pd–CH_2), 2.7 (m, 2 H, Pd–C–CH_2), 4.7—5.3 (m, 2 H, C=CH_2), 6.3 (m, 1 H, CH=C), 6.9—7.9 (m, 20 H, Ph) [d]	
(15) [Rh(η^3-$CH_2CHCHMe$)(η^5-C_5Me_5)I]	1.27 [d, 3 H, CH*Me*, J(HH) 6], 1.56 (s, 15 H, C_5Me_5), 2.79 [d, 1 H, H_a, J(HH) 6], 3.21 (m, 1 H, H_b), 3.87 [d, 1 H, H_s, J(HH) 10], 4.46 (m, 1 H, H_c) [c,d]	
(16) [Rh(η^3-MeCHCHCHMe)(η^5-C_5Me_5)(PPh_3)][BF_4] [e]	1.50 (m, C_5Me_5), 1.64 (br m, Me), 2.34 (m, H_a), 2.70 (m, H_s), 3.96 (m, H_c), 7.53 (m, Ph) [b,c]	9.23 (C_5Me_5), 17.86 (*syn*-Me), 18.14 (*anti*-Me), 66.03 (C–H_a), 70.04 (C–H_s), 92.86 (C–H_c), 102.81 and 106.13 (C_5Me_5), 127.85—134.89 (Ph) [b]

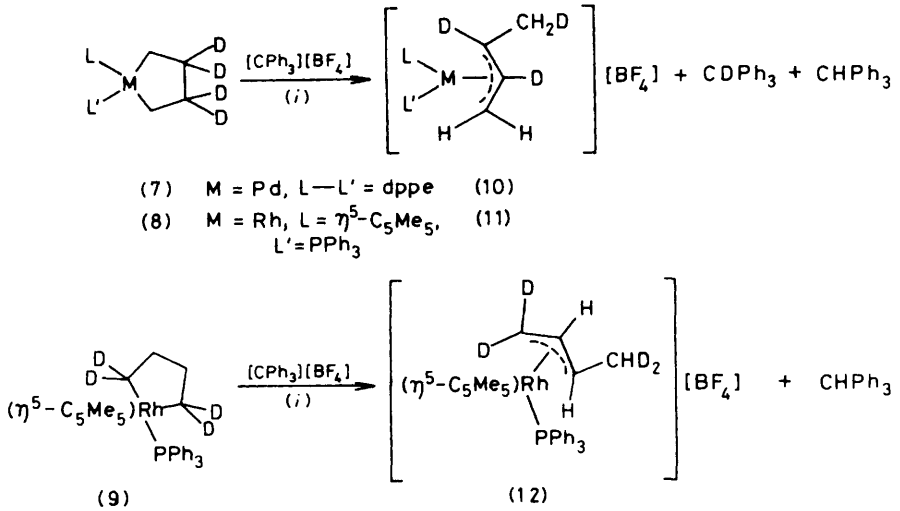
[a] Given as chemical shift (δ), multiplicity, relative intensity, assignment, coupling constants in Hz. br d = broad doublet, br m = broad multiplet. [b] Measured in [$^2H_1$]chloroform, at 37 °C. [c] H_a = *anti*-H, H_b = C*H*Me, H_s = *syn*-H, H_c = central H. [d] Measured in [$^2H_6$]benzene, at 37 °C. [e] Mixture of *syn–syn* and *syn–anti* isomers. ^{31}P N.m.r. spectrum measured in [$^2H_1$]chloroform referenced to H_3PO_4 as external standard: δ 48.36 [d, P(*syn–syn* isomer), J(PRh) 165.86], 42.80 [d, P(*syn–anti* isomer), J(PRh) 168.28 Hz].

alkene compounds.[4] The second step, *i.e.* the isomerization of the σ-3-butenyl system to the η^3-1-methylallyl derivative, has some precedent by analogy with the related iron,[5] ruthenium,[6] nickel,[7] and molybdenum [8] systems. However, since other mechanistic possibilities may be conjectured, we decided to investigate the regiospecificity of the hydrogen abstraction by the trityl cation and the viability of the route leading to cationic π-allylic complexes from σ-3-butenyl compounds.

Deuterium Labelling Studies.—The β,β'-tetradeuteriated pallada- and rhoda-cyclopentane derivatives (7) and (8) were prepared by reacting the appropriate metal dihalide with $LiCH_2CD_2CD_2CH_2Li$, according to the procedures used for the preparation of the corresponding non-deuteriated metallacycles.[2,9,10] The isotopic purity (>95%) of (7) and (8) was evaluated by ^{1}H n.m.r. spectroscopy, and in the case of (8) was confirmed by mass spectrometry [the mass spectrum of (7) does not show the molecular ion].

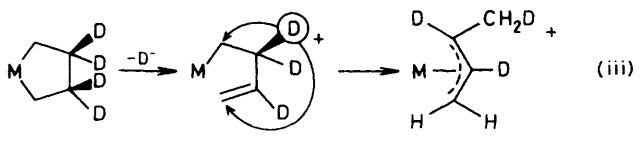
On reaction of (7) and (8) with [CPh_3][BF_4] under the same experimental conditions adopted in the case of the non-deuteriated compounds, the η^3-1-methylallyl derivatives (10) and (11) were respectively obtained (Scheme 2).

The location of the deuterium atoms in the allylic moieties was established by ^{1}H and ^{13}C n.m.r. spectroscopy (Table) by comparing the spectra of the deuteriated and non-deuteriated compounds. In particular, in the ^{13}C n.m.r. spectra the deuteriated carbon atoms were absent owing to increased relaxation time, thus providing a firm structural assignment of deuterium distribution. The triphenylmethane formed in the reaction of (7) with the trityl cation was isolated by t.l.c. and analyzed by mass spectroscopy; it was found to consist of $CDPh_3$ (77%) and $CHPh_3$ (23%). Similarly, the

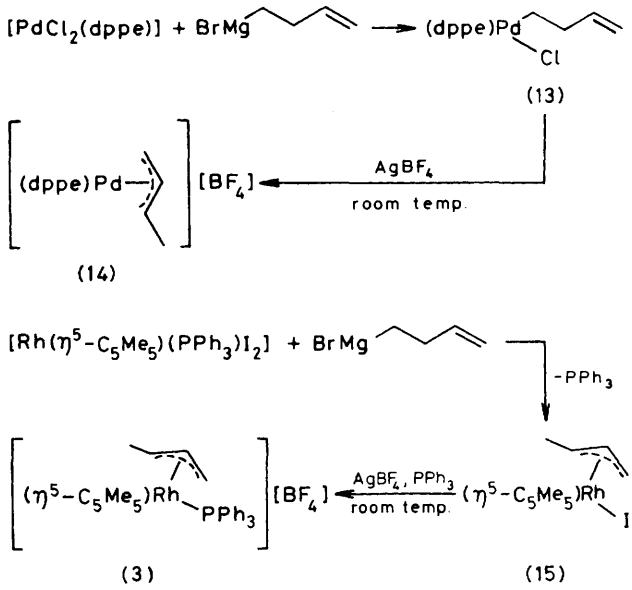


Scheme 2. (*i*) In CH_2Cl_2, room temperature

triphenylmethane recovered from the reaction of the rhodacyclopentane (8) with the trityl cation was found to be a mixture of $CDPh_3$ (71%) and $CHPh_3$ (29%). In addition to possible D/H scrambling processes and some hydrogen abstraction from other sources than the metallacyclic ring, some hydrogen abstraction from the α-positions of the metallacycle could be considered to be responsible for the presence of significant amounts of non-deuteriated triphenylmethane. In order to check this last hypothesis, the α,α'-tetradeuteriated metallacycle (9) was prepared by the reaction of $[Rh(\eta^5\text{-}C_5Me_5)(PPh_3)Cl_2]$ with $LiCD_2CH_2CH_2CD_2Li$ and reacted with $[CPh_3]^+$: we expected that, if a selective β-abstraction reaction occurred, only $CHPh_3$ should form and be detected, due to the absence of a large source of deuterium atoms. Indeed, the η^3-1-methylallyl cationic compound (12) was isolated for which the deuterium distribution shown in Scheme 2 was determined by ^1H and ^{13}C n.m.r. spectroscopy. The mass spectrum of the triphenylmethane formed in this reaction indicated $CDPh_3$ to be present only at natural abundance level, which unambiguously demonstrates that only a β-hydrogen abstraction occurs. Finally, the nature of the deuteriated π-allyl compounds is fully consistent with an origin that envisages a selective β-hydrogen abstraction with the formation of a cationic σ-3-butenyl which rearranges to a η^3-1-methylallyl compound *via* a mechanism in which one of the β-hydrogens is transferred to one of the terminal methylenes: equation (iii). The reliability of this hypothesis is supported by the findings discussed in the following section.

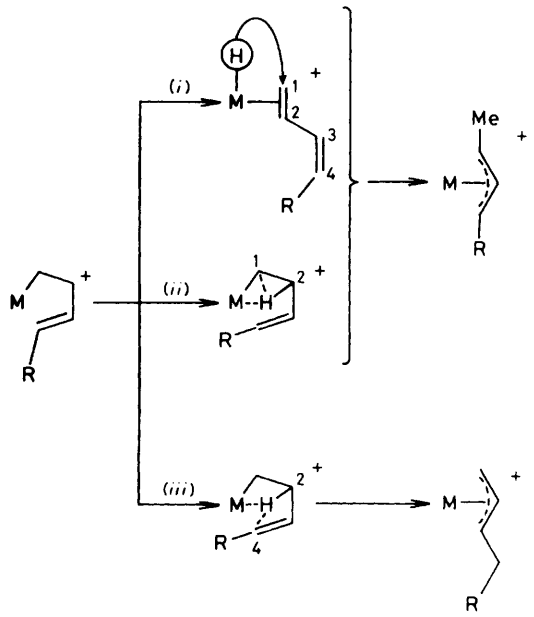


Conversion of σ-3-*Butenyl Complexes to* η^3-1-*Methylallyl Derivatives.*—Thermally or photochemically induced σ-3-butenyl ⟶ η^3-1-methylallyl transformations are well documented in the literature for Fe,[5] Ru,[6] Ni,[7] and Mo[8] compounds. The driving force of the reaction seems to be the detachment of a ligand which causes a co-ordinative unsaturation at the metal centre. To test this possibility and to verify that a facile σ-3-butenyl ⟶ η^3-1-methylallyl rearrangement could occur also in the case of palladium and rhodium compounds, $[Pd(dppe)Cl_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] and $[Rh(\eta^5\text{-}C_5Me_5)(PPh_3)I_2]$ were reacted with 3-butenylmagnesium bromide with the aim of preparing the corresponding mono-σ-3-butenyl derivatives and then removing the halide from the co-ordination sphere of the metal thus creating the conditions for the η^3-1-methylallylic compound to be formed. Indeed, in the case of palladium the reaction leads to the derivative (13) (Scheme 3), in which the double bond of the σ-3-butenyl ligand is not co-ordinated to the metal, as is clearly shown by ^1H n.m.r. spectroscopy (Table).



Scheme 3.

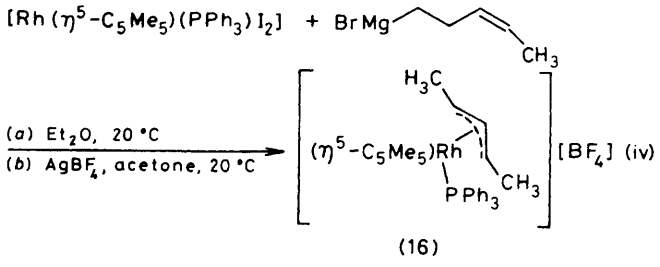
Complex (13) reacts with $AgBF_4$ at room temperature to give immediately (14),[2] in high yields. By reacting $[Rh(\eta^5\text{-}C_5Me_5)(PPh_3)I_2]$ with 3-butenylmagnesium bromide the η^3-1-methylallyl complex (15) is obtained directly (Scheme 3). In this case the loss of the phosphine ligand liberates the co-ordination site necessary for the hydrogen shift to occur. Complex (15) can be converted to (3) by reaction with $AgBF_4$ in the presence of PPh_3, at room temperature.



Scheme 4. R = H or Me

All these reactions demonstrate that σ-3-butenyl compounds are viable intermediates in the trityl-cation promoted metallacyclopentane ⟶ η³-1-methylallyl derivative transformation. How the σ-3-butenyl ⟶ η³-1-methylallyl rearrangement does occur is a more difficult question to answer. In a previous paper [2] we suggested that such a reaction could occur by three pathways (Scheme 4): a β-hydride abstraction followed by addition of M–H to co-ordinated butadiene [reaction (*i*)],[6–8] or alternatively *via* a 2–1 [reaction (*ii*)] or 2–4 [reaction (*iii*)] metal-assisted hydrogen shift.

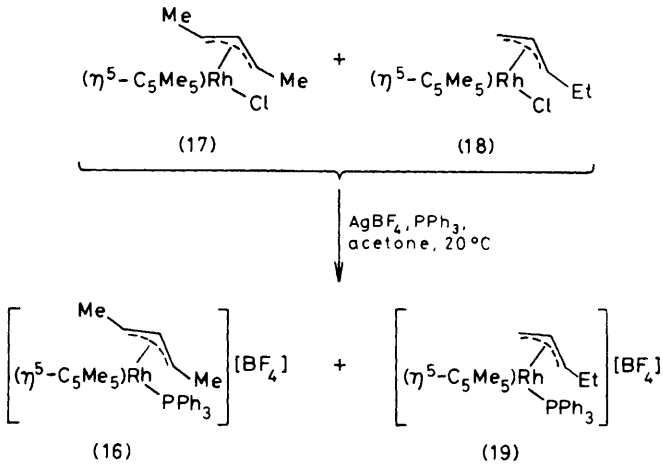
At present we have no data to discriminate between the hydride mechanism and the concerted ones. Furthermore, the deuterium distribution in the π-allyl complexes (10)—(12) (Scheme 2) is exactly that expected, whatever mechanistic pathway is operative. However, when $[Rh(\eta^5\text{-}C_5Me_5)(PPh_3)I_2]$ is treated with 3-pentenylmagnesium bromide a product is obtained which, on reaction with $AgBF_4$, gives a 2.7 : 1 mixture of *syn–syn* and *syn–anti* isomers of the 1,3-dimethylallyl complex (16) [equation (iv)]. Complex (16) has been



(16)

identified by ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy (Table), and by comparing its spectra with those of a 3.5 : 1 mixture of (16) and (19) prepared, according to Scheme 5, from a mixture of the known [11] η³-allyl complexes (17) and (18).

The fact that the σ-3-pentenyl ligand rearranges exclusively to the η³-1,3-dimethylallyl ligand leads to the conclusion that only two of the pathways outlined in Scheme 4 can occur, *i.e.* a hydride abstraction followed by the migration of the hydride to C-1 of co-ordinated 1,3-pentadiene [reaction (*i*)] or,



Scheme 5.

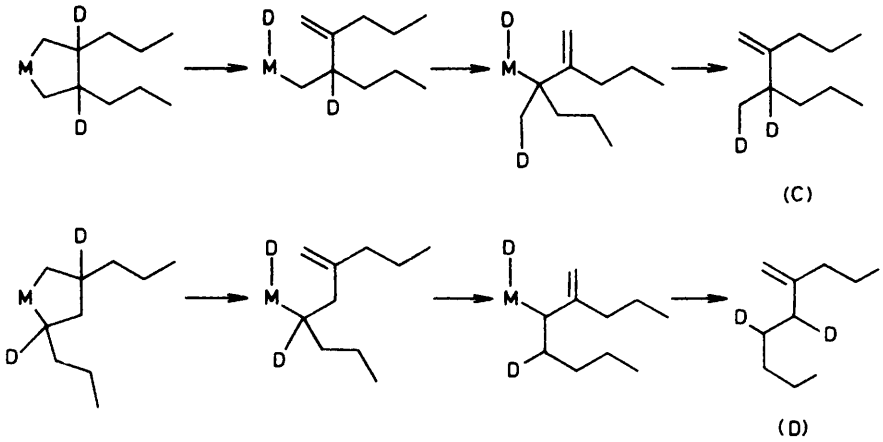
alternatively, a 2–1 rhodium-assisted hydrogen shift [reaction (*ii*)]. In fact, a hydride migration to C-2 or to C-3 does not generate an allyl system, while a hydride migration to C-4 generates a 1-ethylallyl system; analogously a 2–4 rhodium-assisted hydrogen shift would lead to a 1-ethylallyl ligand [Scheme 4, reaction (*iii*)].

All the facts discussed above agree with the idea that the labilization of one β-carbon–hydrogen bond of the σ-3-alkenyl ligand is accomplished through the formation of a two-electron three-centre bond as a result of the interaction of a β-carbon–hydrogen group with the transition metal atom. Necessary conditions for the occurrence of such an interaction are the requirement of a co-ordinatively unsaturated metal centre [12] and the ability of the alkyl–metal system to achieve the most favourable M–C–C–H dihedral angle. Indeed, a survey of the literature shows that the σ-3-butenyl ⟶ 1-methylallyl rearrangement takes place when a co-ordinative unsaturation is present at the metal atom, which can be induced by thermal [6–8] or photochemical [5] labilization of a neutral ancillary ligand or, alternatively, as has been shown in the present work, by removing an anionic ligand. Moreover, the σ-3-butenyl ligand must be conformationally free; no rearrangement has been observed in the case of crowded and rigid homoallylic systems such as σ-η-norbornenyl complexes.[13]

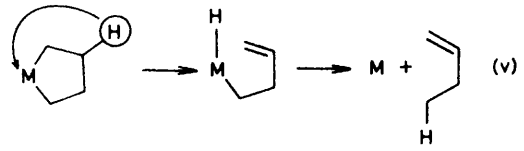
Conclusions

The reactions described herein provide a basis for examining the metallacyclopentane ⟶ 1-methylallyl derivative transformation induced by the trityl cation as a general feature of metallacyclopentane compounds. All evidence strongly supports a mechanism in which the predominant reaction pathway involves a β-hydrogen abstraction followed by a fast rearrangement of a σ-3-butenyl intermediate.

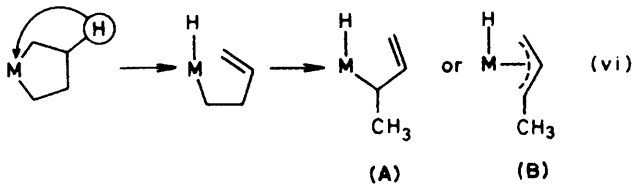
In the case of transition-metal linear alkyls the β-hydrogen abstraction reaction by the trityl cation appears to be related to the ubiquitous β-hydrogen elimination reaction. Similarly, this study has defined some conceptual analogies between the reaction of metallacyclopentanes with the trityl cation and the important metallacyclopentane ⟶ σ-3-butenyl metal hydride reaction that so frequently has been proposed as the key step in the formation of butenes from metallacyclopentanes: [1] equation (v). In other words, we are inclined to believe that a σ-3-butenyl ⟶ 1-methylallyl rearrangement can occur also in those cases where a σ-3-butenyl metal hydride is generated; the overall metallacyclopentane ⟶



Scheme 6.



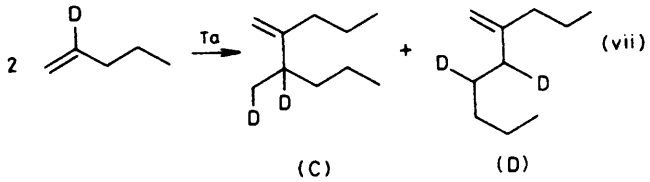
1-methylallyl metal hydride transformation [equation (vi)] may well be a feature of the chemistry of metallacyclopentanes.



Observations and hypotheses such as those discussed above turned our attention to the possibility of extending these ideas to a reinterpretation of other published data. For example, it is known that metallacyclopentanes thermally decompose in several ways including the formation of 1- and 2-butenes.[1] While a reaction pathway such as that shown in equation (v) accounts well for the formation of an α-olefin, $R-CH=CH_2$, the appearance of an internal olefin, $R-CH=CH-R'$, has been accounted for by the isomerization of the initially formed α-olefin.[14-16] In particular, according to Whitesides and co-workers [14] all the olefinic products deriving from platinum(II) metallacyclopentanes are presumably formed by metal–hydride additions and eliminations before the olefin is released into solution.

These findings could be nicely explained assuming that the reaction pathway outlined in equation (vi) takes place followed by reductive elimination of olefin: intermediate (A) will give rise to 1-butene, while intermediate (B) will give rise to 1-butene or *cis*- and *trans*-2-butene depending upon the regioselectivity of hydrogen migration and upon the relative concentrations of *syn*- and *anti*-1-methylallyl complexes.

Furthermore, Schrock and co-workers [17] have demonstrated that some tantalum-catalyzed linear dimerizations of α-olefins proceed *via* tantalacyclopentane intermediates. In particular, deuterium-labelling studies have shown that the most immediate mechanism, *i.e.* a β-hydrogen elimination–reductive elimination sequence could account only for dimer (C), the presence of dimer (D) remaining unexplained [equation (vii)].[17]



The formation of both these dimers has been explained through a ring-contraction pathway following an intramolecular β-hydrogen elimination reaction.[17]

We wish to draw attention to the observation that the same dimers could be explained by the alternative pathway (Scheme 6) involving 'concerted' fast isomerization of an intermediate σ-3-butenyl metal hydride to a 1-methylallyl metal hydride. This hypothesis has some advantages over the ring-contraction mechanism. First, it does not require that the head-to-tail dimer (D) forms *via* an initial secondary β-hydrogen abstraction, but in both cases a tertiary β-hydrogen is initially abstracted. Secondly, a study of the thermal decomposition of 2,2,3-trisubstituted platinacyclobutanes has shown that two types of β-abstraction are operative: a β-hydrogen abstraction from the ring and a β-hydrogen abstraction from a α-methyl group, the latter being favoured.[18]

In conclusion, because in the absence of labelling marks the mechanisms proposed [1] for the degradation of metallacycles to olefins having the same number of carbon atoms are indistinguishable, it is possible that the involvement of the metallacyclopentane ⟶ 1-methylallyl metal hydride reaction in the general reactivity of this class of compounds is much more common than hitherto suspected.

Work is in progress to obtain further evidence on this point.

Experimental

All reactions and manipulations of organometallics were carried out under dinitrogen or argon. The solvents were dried and distilled. The compounds $[PdCl_2(dppe)]$,[19] $[Rh(\eta^5\text{-}C_5Me_5)(PPh_3)X_2]$ (X = Cl or I),[20] $[Rh(CH_2CH_2CH_2CH_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$,[10] $[Ir(CH_2CH_2CH_2CH_2)(\eta^5\text{-}C_5Me_5)(PPh_3)]$,[9] $LiCH_2CD_2CD_2CH_2Li$,[21] $MgBr(CH_2CH_2CHCH_2)$,[22] $MgBr(CH_2CH_2CHCHMe)$,[23] and $[CPh_3][BF_4]$ [24] were prepared as described previously. Hydrogen-1 n.m.r. spectra were run at 60 MHz on a Varian T60 spectrometer and at 100 MHz on a Varian

XL100 instrument by using $SiMe_4$ as internal standard. Carbon-13 n.m.r. spectra were run on a Varian XL100 instrument. Mass spectra were obtained with a Varian MAT CH7 spectrometer. I.r. spectra were run on a Perkin-Elmer 238-B instrument. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

Reaction of (1) *with* $[CPh_3][BF_4]$: *Formation of* (η^3-1-*Methylallyl*)(η^5-*pentamethylcyclopentadienyl*)(*triphenylphosphine*)*rhodium*(III) *Tetrafluoroborate*, (3).—Compound (1) (0.11 g, 0.198 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and $[CPh_3][BF_4]$ (0.064 g, 0.195 mmol) in CH_2Cl_2 (3.3 cm^3) was added dropwise with stirring. The resulting red-orange solution was added to diethyl ether (70 cm^3) and a yellow solid precipitated. The precipitate was filtered off and washed repeatedly with diethyl ether, yield 0.122 g (97%) (Found: C, 59.95; H, 6.00; P, 5.10. Calc. for $C_{32}H_{37}BF_4PRh$: C, 59.85; H, 5.80; P, 4.80%).

Reaction of (2) *with* $[CPh_3][BF_4]$: *Formation of* (η^3-1-*Methylallyl*)(η^5-*pentamethylcyclopentadienyl*)(*triphenylphosphine*)*iridium*(III) *Tetrafluoroborate*, (4).—A similar reaction between (2) (0.127 g, 0.197 mmol) and $[CPh_3][BF_4]$ (0.057 g, 0.173 mmol) in CH_2Cl_2 (3 cm^3) gave pale yellow crystals of (4), yield 0.108 g (85%) (Found: C, 52.2; H, 5.15; P, 4.70. Calc. for $C_{32}H_{37}BF_4IrP$: C, 52.25; H, 5.10; P, 4.60%).

Preparation of $LiCD_2CH_2CH_2CD_2Li$.—[$^2H_4$]Butane-1,4-diol was prepared (yield 8 g, 36%) from $CH_3OC(O)CH_2CH_2C(O)OCH_3$ (Fluka) by reduction with $LiAlD_4$ (C.E.A., isotopic purity 99%) in diethyl ether. $ClCD_2CH_2CH_2CD_2Cl$ [b.p. 56—61 (17 mmHg); ^1H n.m.r., δ 1.9 p.p.m. (m); isotopic purity 99%] was obtained in 41% yield after treatment of the corresponding alcohol with $SOCl_2$ in benzene. Reaction of the dichloride with lithium in diethyl ether at 0 °C yielded the product (yield 65%).

[Pd($CH_2CD_2CD_2CH_2$)(dppe)] (7).—Following the same procedure reported for the non-deuteriated compound,[2] [$PdCl_2$(dppe)] (0.5 g, 0.86 mmol) suspended in diethyl ether (40 cm^3) was reacted with $LiCH_2CD_2CD_2CH_2Li$ (2.65 mmol; 7.38 cm^3 of a 0.36 mol dm^{-3} diethyl ether solution) to give 0.18 g of (7) (36%).

[Rh($CH_2CD_2CD_2CH_2$)(η^5-C_5Me_5)(PPh_3)] (8).—Following the same procedure reported for (1),[10] [Rh(η^5-C_5Me_5)(PPh_3)Cl_2] (0.3 g, 0.525 mmol) supended in diethyl ether (70 cm^3) was reacted with $LiCH_2CD_2CD_2CH_2Li$ (1.62 mmol; 4.5 cm^3 of a 0.36 mol dm^{-3} diethyl ether solution) to give 0.064 g of (8) (22%). Mass spectrum: *m/e* 560 (*P*).

[Rh($CD_2CH_2CH_2CD_2$)(η^5-C_5Me_5)(PPh_3)] (9).—Following the usual procedure, [Rh(η^5-C_5Me_5)(PPh_3)Cl_2] (0.3 g, 0.525 mmol) in diethyl ether (70 cm^3) was reacted with $LiCD_2CH_2CH_2CD_2Li$ (1.60 mmol; 5.6 cm^3 of a 0.285 mol dm^{-3} diethyl ether solution) to give 0.062 g (22%) of (9) (99% isotopic purity). Mass spectrum: *m/e* 560 (*P*).

Reaction of [Rh($CH_2CD_2CD_2CH_2$)(η^5-C_5Me_5)(PPh_3)] (8) *with* $[CPh_3][BF_4]$.—The reaction was run in the same way as for the non-deuteriated metallacycle using (8) (0.054 g, 0.096 mmol) in CH_2Cl_2 (1.5 cm^3) and $[CPh_3][BF_4]$ (0.031 g, 0.094 mmol) in CH_2Cl_2 (2 cm^3). After precipitation of [Rh(η^3-$CH_2CDCDCH_2D$)(η^5-C_5Me_5)(PPh_3)][BF_4] (11) (0.041 g, 66%), the ethereal solution was filtered, then concentrated and applied to a preparative silica-gel t.l.c. plate which was then eluted with n-hexane. The u.v.-active triphenylmethane band was isolated and extracted with CH_2Cl_2. Analysis of the *m/e* 244 : 245 peak ratio in the mass spectrum (10 eV) indicated a ratio of 71 : 29 for $CDPh_3$: $CHPh_3$.[25]

Reaction of [Rh($CD_2CH_2CH_2CD_2$)(η^5-C_5Me_5)(PPh_3)] (9) *with* $[CPh_3][BF_4]$.—The reaction was run as above, using 0.084 g of (9) (0.15 mmol) in CH_2Cl_2 (2.3 cm^3) and $[CPh_3][BF_4]$ (0.049 g, 0.15 mmol) in CH_2Cl_2 (2.2 cm^3) to give 0.083 g (87%) of [Rh(η^3-$CD_2CHCHCD_2H$)(η^5-C_5Me_5)(PPh_3)][BF_4] (12) and $CHPh_3$ (>99% isotopic purity).

Reaction of [Pd($CH_2CD_2CD_2CH_2$)(dppe)] (7) *with* $[CPh_3][BF_4]$.—The reaction was carried out in the same way as for the non-deuteriated compound,[2] using 0.180 g of (7) (0.318 mmol) in CH_2Cl_2 (2 cm^3) and $[CPh_3][BF_4]$ (0.105 g, 0.318 mmol) in CH_2Cl_2 (6 cm^3). [Pd(η^3-$CH_2CDCDCH_2D$)(dppe)][BF_4] (10) (0.202 g, 97% yield) was obtained together with triphenylmethane (ratio $CDPh_3$: $CHPh_3$ of 77 : 23).

Reaction of [$PdCl_2$(dppe)] *with* $MgBr(CH_2CH_2CHCH_2)$: *Formation of* [Pd(σ-$CH_2CH_2CHCH_2$)Cl(dppe)] (13).—To a suspension of [$PdCl_2$(dppe)] (0.309 g, 0.537 mmol) in diethyl ether (30 cm^3) was added $MgBr(CH_2CH_2CHCH_2)$ (2.38 mmol; 5 cm^3 of a 0.476 mol dm^{-3} diethyl ether solution), at −70 °C. The reaction mixture was kept at −70 °C for 20 min then the temperature was slowly raised to 20 °C and the reaction mixture stirred for 1 h. The mixture was hydrolyzed with dilute HCl; the ethereal layer and the combined ethereal extracts were dried over anhydrous Na_2SO_4, then evaporated to dryness. A pale yellow solid was obtained (0.15 g, yield 47%) (Found: C, 59.2; H, 4.85; Cl, 5.20; P, 10.00. Calc. for $C_{30}H_{31}ClP_2Pd$: C, 60.3; H, 5.20; Cl, 5.95; P, 10.70%).

Reaction of [Pd(σ-$CH_2CH_2CHCH_2$)Cl(dppe)] (13) *with* $AgBF_4$: *Formation of* [Pd(η^3-$CH_2CHCHMe$)(dppe)][BF_4] (14).—To a solution of (13) (0.15 g, 0.252 mmol) in acetone (10 cm^3), a solution of $AgBF_4$ (0.048 g, 0.252 mmol) in acetone (5 cm^3) was slowly added dropwise. The resulting dark red solution was stirred for 30 min at room temperature and then evaporated to dryness. The residue was dissolved in CH_2Cl_2, filtered, and poured into diethyl ether (150 cm^3). A precipitate formed which was washed repeatedly with diethyl ether and dried under vacuum to give (14) (0.136 g, yield 84%), identified by comparison of its properties with those of an authentic sample.[2]

Reaction of [Rh(η^5-C_5Me_5)(PPh_3)I_2] *with* $MgBr(CH_2CH_2CHCH_2)$: *Formation of* [Rh(η^3-$CH_2CHCHMe$)(η^5-C_5Me_5)I] (15).—To a stirred suspension of [Rh(η^5-C_5Me_5)(PPh_3)I_2] (0.3 g, 0.398 mmol) in diethyl ether (60 cm^3), $MgBr(CH_2CH_2CHCH_2)$ (0.807 mmol; 1.7 cm^3 of a 0.475 mol dm^{-3} diethyl ether solution) was added at room temperature. The mixture was stirred for 4 h giving a red solution and a white precipitate. The mixture was treated with aqueous NH_4Cl and the ethereal layer was dried over anhydrous Na_2SO_4 and then evaporated to dryness under vacuum. The residue was extracted with n-pentane (3 × 30 cm^3), and the collected extracts were filtered, ethanol added (3.5 cm^3), and concentrated to 15 cm^3. After cooling at −30 °C, red crystals of (15) were obtained (0.045 g, 27%) (Found: C, 40.65; H, 5.20; I, 29.45. Calc. for $C_{14}H_{22}IRh$: C, 40.0; H, 5.30; I, 30.2%). *M* (in benzene, by osmometry) = 429 (calc.: 420.14).

Reaction of [Rh(η^3-$CH_2CHCHMe$)(η^5-C_5Me_5)I] (15) *with* $AgBF_4$ *and* PPh_3: *Formation of* (3).—To a solution of (15) (0.06 g, 0.143 mmol) and PPh_3 (0.038 g, 0.154 mmol) in acetone (10 cm^3), was added $AgBF_4$ (0.030 g, 0.154 mmol) in acetone (3.1 cm^3). A rapid reaction took place and a precipitate formed. After stirring for 20 min, the suspension was filtered and the solution evaporated to dryness. The residue was dissolved in CH_2Cl_2 (3 cm^3) and the solution was poured in diethyl ether (80 cm^3) to give (3) (0.09 g, 98%).

Reaction of [Rh(η^5-C_5Me_5)(PPh_3)I_2] *with* $MgBr(CH_2CH_2CHCHMe)$, *then with* $AgBF_4$: *Formation of* [Rh(η^3-MeCHCHCHMe)(η^5-C_5Me_5)(PPh_3)][BF_4] (16).—To a suspension of [Rh(η^5-C_5Me_5)(PPh_3)I_2] (0.4 g, 0.531 mmol) in diethyl ether (50 cm^3), $MgBr(CH_2CH_2CHCHMe)$ (2.12 mmol; 4 cm^3 of a 0.53 mol dm^{-3} diethyl ether solution) was added dropwise during 20 min, at room temperature. The mixture was stirred for another 4 h, then hydrolyzed with 10% aqueous NH_4Cl (15 cm^3). A yellow solid formed at the interface which was separated and dried under vacuum. This solid was treated with acetone (10 cm^3) which caused the precipitation of a mixture of NH_4Cl and MgBrI. The supernatant solution was separated and treated with a solution of $AgBF_4$ (0.023 g, 0.118 mmol) in acetone (3 cm^3). After stirring for 20 min the mixture was filtered and the pale red solution was evaporated to dryness under vacuum. The residue was dissolved in CH_2Cl_2 (8 cm^3) and the solution poured into diethyl ether (80 cm^3) to give (16) (0.0333 g, 44%) as a yellow microcrystalline solid (Found: C, 60.3; H, 5.95; P, 4.60. Calc. for $C_{33}H_{39}BF_4PRh$: C, 60.4; H, 6.00; P, 4.70%).

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