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TRANSITION METAL BUTADIENYL COMPLEXES

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CONTENTS

1. INTRODUCTION

The chemistry of transition metal allyl complexes has been well developed in the last few decades. Much of the impetus for studies on η^1- and η^3-allyl systems relates to their facile conversion to metal-coordinated alkenes and dienes, and hence their direct and indirect use in organic synthesis

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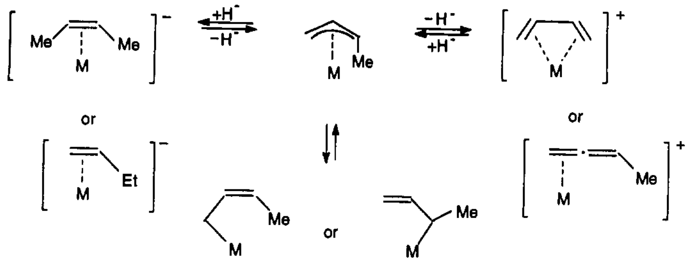
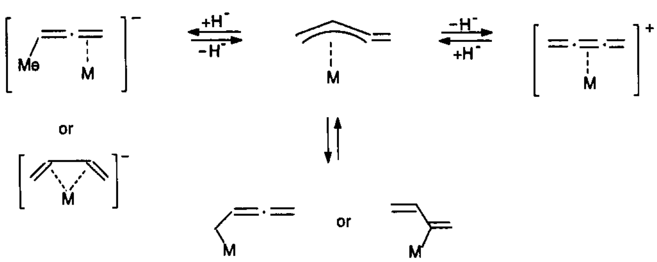


Scheme 1.

(Scheme 1). For example, the manipulation of steric and electronic effects in η^3-allyl metal intermediates has resulted in transition metal catalysed allylations emerging as a set of extremely powerful and versatile reactions, which now include highly enantioselective catalytic allylic alkylations.[1] Concomitant with these developments has been an improved understanding and recognition of the novel structure, bonding, dynamic properties and reactivity patterns exhibited by this class of compounds. Of prime importance in many dynamic processes is the $\eta^3 \rightarrow \eta^1$-rearrangement, and as each carbon atom in the C_3 backbone is potentially a stereogenic centre, an exact knowledge of the behaviour of the metal–allyl link under a well-defined set of conditions is also of synthetic relevance.[2]

In contrast to the well-developed chemistry of the allyl ligand, the chemistries of other π-enyl systems which are of interest as organic synthons, have been comparatively neglected. One such system is based on the η^3-butadienyl ligand, which can in principle undergo a $\eta^3 \rightarrow \eta^1$-rearrangement



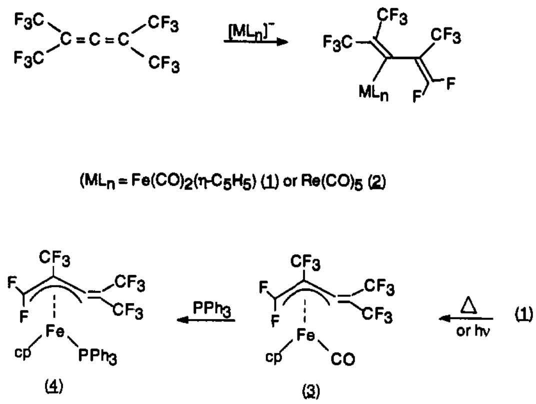
Scheme 2.

and bears a simple formal relationship to allenes, butadienes and butatrienes (Scheme 2). Our intention in this review is to survey the known chemistry of 2-η^1- and 1,2,3-η^3-butadienyl complexes, and compare their properties with those of corresponding allyl derivatives. In the final section we focus attention to their potential use as synthons.

2. HISTORICAL

The first complex containing an η^3-butadienyl ligand was reported by Nesmeyanov and coworkers in 1976.[3,4] They showed that nucleophilic attack by the metal carbonylate anions $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ and $[Re(CO)_5]^-$ on the electrophilic central carbon atom of 1,1,3,3-tetrakis(trifluoromethyl)allene produced initially η^1-butadienyl complexes (**1**) and (**2**) which in the case of the iron complex underwent thermal or photolytic decarbonylation to give the η^3-butadienyl derivative $Fe(\eta\text{-}C_5H_5)(CO)(\eta^3\text{-}F_2CC(CF_3)C{=}C(CF_3)_2)$ (**3**). Photolysis of (**3**) in the presence of PPh_3 yielded the non-carbonyl containing phosphine analogue $Fe(\eta\text{-}C_5H_5)(PPh_3)(\eta^3\text{-}F_2CC(CF_3)C{=}C(CF_3)_2)$ (**4**) (Scheme 3). The structures of (**2**) and (**4**) were established by X-ray crystallography. Later in the same year, Giering[5] reported the isolation of low yields of $Fe(\eta\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C({=}CH_2)CH{=}CH_2)$ (**5**) from the reaction of 1,4-dichloro-2-butyne with the $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ anion.

It is interesting to note that photolytic or thermal decarbonylation of (**2**) to form an analogous η^3-butadienyl complex could not be achieved.[3] This was accounted for by the greater stability of the Re—CO bond. A parallel can be drawn here with the analogous conversion of $Re(\eta^1\text{-}C_3H_5)(CO)_5$ to $Re(\eta^3\text{-}C_3H_5)(CO)_4$, which for several years could not be accomplished until the correct experimental



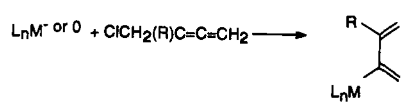
Scheme 3.

conditions were determined.[6] Subsequently a number of η^1- and η^3-butadienyl complexes, both neutral and charged, have been prepared via the synthetic routes detailed in sections 3.1–3.5.

3. PREPARATIVE ROUTES FOR TRANSITION METAL 2-η^1- AND 1,2,3-η^3-BUTADIENYL COMPLEXES

3.1. *Via allenes*

In addition to the Fe and Re complexes discussed above, both Welker and co-workers[7–9] and Green and co-workers[10–12] have isolated 2-η^1-butadienyl complexes from the reaction of metal salts with 4-chloro- or 4-tosyl-1,2-butadienes. Clean S_N2' halide replacement reactions occur with anionic Co and Fe species, whereas oxidative–addition to neutral Pt^0 and Pd^0 is preferred (Scheme 4).

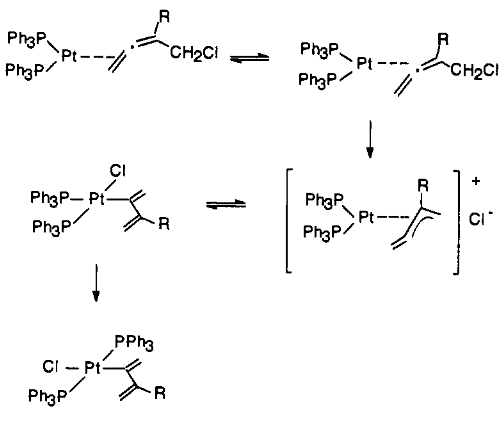


R = H, L_nM = Fe(η-C_5H_5)$(CO)_2$ (5), Co(4-t-Bupy)$(dmg)_2$ (6), Co(py)$(dmg)_2$ (7) Co(2,6-Me_2py)$(dmg)_2$ (8); R = Me, L_nM = ClPt(dppf) (9), ClPt$(PPh_3)_2$ (10), ClPt(dppe) (11), ClPd$(PPh_3)_2$ (12); R = Et, L_nM = ClPt$(PPh_3)_2$ (13), ClPt(dppf) (14), ClPd$(PPh_3)_2$ (15).

Scheme 4.

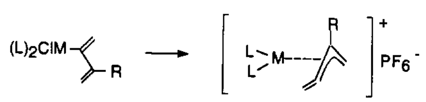
Complexes (**6**), (**8**) and (**14**) have been structurally characterized by X-ray crystallography. The Co complexes (**6**) and (**8**) show an approximately *s-cis* conformation of the 2-metal substituted-1,3-butadiene fragment[7–9] but with torsion angles C=C—C=C of 54° and 63°, respectively, which are large compared to *s-cis* dienes in general, but much smaller than the value of 83° found in (**2**). However, in the Pt complex (**14**), an almost planar *s-trans* conformation (torsion angle 5.8°) is found for the C_4 skeleton.[12] A more detailed description of these structures and those of their analogues is given in Section 4.1. NMR evidence for the intermediacy of a *cis*-2-η^1-butadienyl complex during the formation of (**13**) was obtained in this same study,[12] and a mechanism was proposed in which the PtL_2 (L = PPh_3) fragment transfers from the unsubstituted double bond (Scheme 5), prior to the oxidative–addition step.

Treatment of (2-η^1-butadienyl)Pt^{II} or Pd^{II} complexes with $AgPF_6$ or $TlPF_6$ affords 1,2,3-η^3-butadienyl analogues in high yields (Scheme 6). The structure of (**20**) was confirmed by a crystallographic study.[12] A similar $\eta^1 \rightarrow \eta^3$-transformation can be effected on (**5**), either by photolysis or reaction with trialkyl phosphites or phosphines.[8] By contrast, the reaction of the $[Co(PPh_3)(CO)_3]^-$ anion with 5-(*p*-toluenesulfonyl)-2-methyl-2,3-pentadiene yields an η^3-butadienyl derivative $Co(PPh_3)(CO)_3(\eta^3\text{-}H_2CCHC{=}CH_2)$ (**23**) whereas 4-(*p*-toluenesulfonyl)-1,2-butadiene reacts with this anion, and with $[M(\eta\text{-}C_5H_5)(CO)_3]^-$ (M = Mo, W), to yield various CO insertion products but no butadienyl complexes.[8]



(13)

Scheme 5.



R = H, ML_2 = $Pt(PPh_3)_2$ (16), Pt(dppf) (17); R = Me, ML_2 = $Pt(PPh_3)_2$ (18), Pt(dppf) (19); R = Et, ML_2 = $Pt(PPh_3)_2$ (20), Pt(dppf) (21), $Pd(PPh_3)_2$ (22).

Scheme 6.

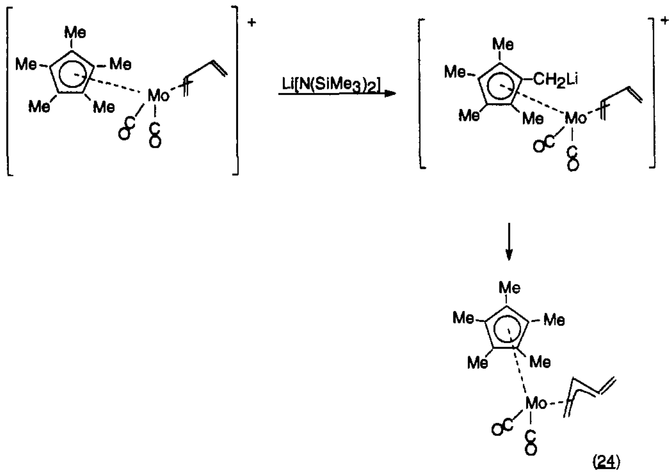
3.2. *From* 1,3-*butadienes*

The most direct entry into butadienyl complexes involves the intermediacy of 1,3-butadiene derivatives, and metallation of the C_2 atom can be achieved in several ways. Tada and Shimizu[13] prepared the Co-η^1-butadienyl complex (**7**) from $CoCl(dmg)_2(py)$ (dmg, dimethylglyoximate anion; py = pyridine) and the Grignard reagent prepared from 2-chloro-1,3-butadiene, and many of the square planar Pt^{II}– and Pd^{II}–(2-η^1-butadienyl) complexes prepared using 4-chloro-1,2-butadienes are also available from analogous reactions employing 2-chloro-1,3-butadiene.[11] Both deprotonation and desilylation of cationic η^4-butadiene complexes affords a convenient route to 1,2,3-η^3-butadienyl derivatives of a range of metals. Deprotonation of $[Mo(\eta\text{-}C_5Me_5)(CO)_2(\eta^4\text{-butadiene})]BF_4$ with $Li[N(SiMe_3)_2]$ gave a low yield of the η^3-butadienyl analogue via an unusual reaction which deuteration studies showed to involve the initial deprotonation of a methyl group on the η-C_5Me_5 ligand (Scheme 7).[14] Better yields for complex (**24**) and for many other carbonyl containing metal systems were obtained using desilylation of 2-silyl substituted η^4-1,3-butadiene species (Scheme 8).[14,15] Complexes (**24**) and (**25**) were the first containing the unsubstituted η^3-butadienyl ligand to be characterized by X-ray crystallography.

3.3. *By ring-opening reactions*

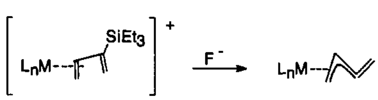
A novel ring-opening reaction of a cyclopropenyl ligand led to the first cationic η^3-butadienyl complex of Pt, $[(Ph_3P)_2Pt(\eta^3\text{-}Ph(H)CC(Ph)C{=}CH_2)]BF_4$ (**26**), which is formed by the action of $Pt(PPh_3)_2(C_2H_4)$ on the methyldiphenylcyclo-propenyl cation via a ring-opening reaction coupled with a hydrogen shift.[16] Some of the key stages in a possible mechanism are outlined in Scheme 9.

Bruce and co-workers[17–22] have also applied ring-opening procedures to prepare a range of both 2-η^1-butadienyl and η^3-butadienyl complexes by reacting metal σ-acetylide complexes with electron deficient olefins. σ-Cyclobutenyl products resulting from a [2+2] cycloaddition reaction may be isolated in some reactions, and these compounds subsequently undergo slow conversion to η^1- and/or η^3-butadienyl derivatives (Scheme 10). Cycloaddition of *trans*-$CH(CO_2Me){=}C(CN)(CO_2Me)$ with $Ru(C_2Ph)(\eta\text{-}C_5H_5)(CO)(PPh_3)$ afforded two isomers of the cyclobutenyl complex



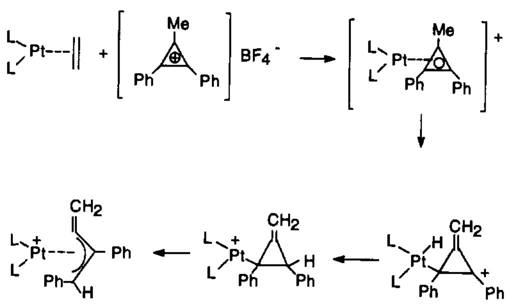
(24)

Scheme 7.



$L_nM = Fe(\eta\text{-}C_5H_5)(CO)$ (5), $Mo(\eta\text{-}C_5Me_5)(CO)_2$ (24), $Ru(\eta\text{-}C_5H_5)(CO)$ (25).

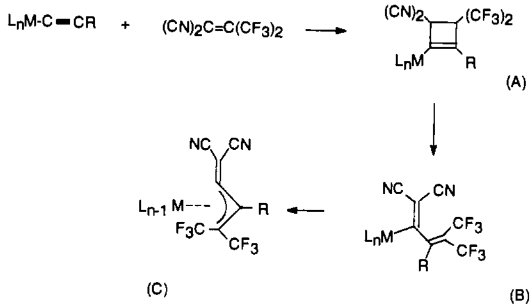
Scheme 8.



Scheme 9.

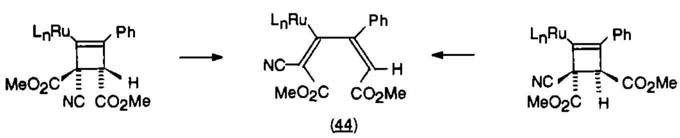
$Ru\{C{=}C(Ph)CH(CO_2Me)C(CN)(CO_2Me)\}(\eta\text{-}C_5H_5)(CO)(PPh_3)$ formed by approach of the acetylide to each side of the alkene plane.[23] Thermal opening of the cyclobutenyl ring occurred in conrotatory fashion in both products to give the same η^1-butadienyl complex (**44**), indicating that the transition metal substituent does not affect the course of the reaction, which is in accord with the Woodward–Hoffmann rules (Scheme 11). Thermolysis of (**44**) resulted in PPh_3 rather than CO loss, and formation of $Ru\{\eta^3\text{-}CH(CO_2Me)C(Ph)C{=}C(CN)(CO_2Me)\}(\eta\text{-}C_5H_5)(CO)$ (**45**). Other Ru-η^1-butadienyl complexes in this series include $Ru\{C({=}C(CN)_2)C(Ph){=}C(CN)_2\}(\eta\text{-}C_5H_5)(L_2)$ [L_2 = dppe, 1,2-bis(diphenylphosphino)ethane (**46**); PPh_3, $CNBu^t$ (**47**); PPh_3, CO (**48**)] of which (**48**) undergoes photolytic decarbonylation to afford the expected η^3-butadienyl derivative (**49**), which can be readily converted back to (**48**) by the addition of CO. Bruce *et al.*[24] have also shown that the reaction between some 1-alkynes and η^1-vinyl derivatives of Ru affords η^3-butadienyl complexes directly (Scheme 12).

In studies on (η^1-4-alkylidene-1-silacyclobutenyl)Pt^{II} complexes, Lukehart and co-workers[25,26] have shown that if the reaction leading to this four-membered heterocycle is carried out in the presence of water or alcohol, (η^3-butadienyl)Pt^{II} complexes containing a $R_2Si(OH)$ or $R_2Si(OR)$ substituent at the central position of the allyl fragment are formed. In a revised mechanism, a cationic η^1-alkenylidene complex rather than a silacyclobutenyl intermediate is favoured as the

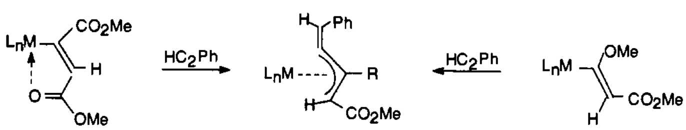


(A): R = Ph, L_nM = W(η-C_5H_5)$(CO)_3$ (27), Fe(η-C_5H_5)$(CO)_2$ (28), $Mn(CO)_3$(dppe) (29), Ru(η-C_5H_5)(CO)(PPh_3) (30), Ru(η-C_5H_5)$(PPh_3)_2$ (31), Ru(η-C_5H_5)(dppe) (32); R = Me, L_nM = Ru(η-C_5H_5)$(PPh_3)_2$ (33), Ru(η-C_5H_5)(CO)(PPh_3) (34); (B): R = Ph, L_nM = W(η-C_5H_5)$(CO)_3$ (35), Ni(η-C_5H_5)$(PPh_3)_2$ (36), Ru(η-C_5H_5)(CO)(PPh_3) (37), Ru(η-C_5H_5)$(PPh_3)_2$ (38), Ru(η-C_5H_5)(dppe) (39); R = Me, L_nM = Ru(η-C_5H_5)(CO)(PPh_3) (40), Ru(η-C_5H_6)$(PPh_3)_2$ (41); (C): R = Ph, $L_{n-1}M$ = W(η-C_5H_5)$(CO)_2$ (42), Ru(η-C_5H_5)(PPh_3) (43).

Scheme 10.



Scheme 11.



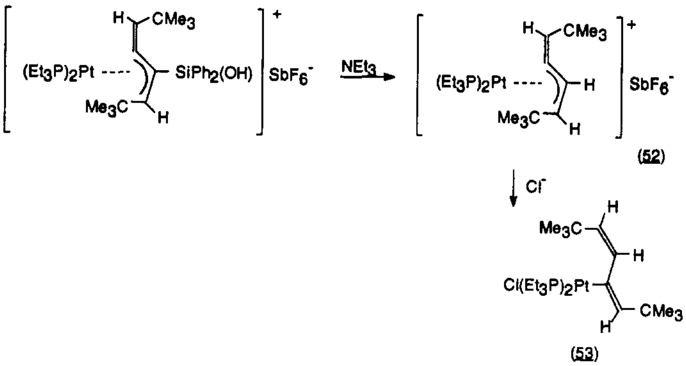
L_nM = Ru(η-C_5H_5)(PPh_3), R = CO_2Me (50) or OMe (51)

Scheme 12.

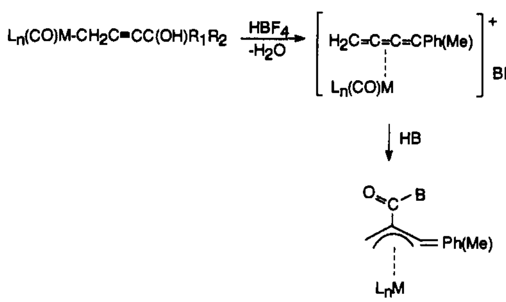
butadienyl precursor.[26] Treatment of one of these salts with NEt_3 results in elimination of the Si substituent and replacement with H. An $\eta^3 \rightarrow \eta^1$ conversion can be affected by excess Cl^- (Scheme 13).[26]

3.4. *From butatrienes and acetylenes*

Several cationic η^2-butatriene complexes are available via protonation and then dehydration of the alcohol function in $M'CH_2C{\equiv}CC(OH)R_1R_2$ (M′ = Mo(η-C_5H_5)$(CO)_3$ or Fe(η-C_5H_5)$(CO)_2$).[27] Both the stability and reactivity towards nucleophiles of the resultant cations depend upon the metal used and on the substituents R_1 and R_2, but several can be converted to neutral η^3-butadienyl derivatives by reaction with methoxide ion, $NHEt_2$ or NH_2Et (Scheme 14).[27] The same authors showed that double addition of methanol of Mo(η-C_5H_5)$(CO)_3$(η^1-$CH_2C{\equiv}CC{\equiv}CMe$) also yields an η^3-butadienyl product.[28] The first addition, with CO insertion gives an η^3-allyl-alkoxycarbonylated product, and subsequent catalysed 1,5-methanol addition to this intermediate yields $Mo(C_5H_5)(CO)_2$(η^3-$C(CH_2OMe)(CO_2Me)CHC{=}CHMe$) (**58**). An Fe($\eta$-$C_5H_5$)(CO) analogue (**59**) of this same ligand system was prepared by a variation of this route which involved the intermediacy of a η^4-vinylallene species.[28]



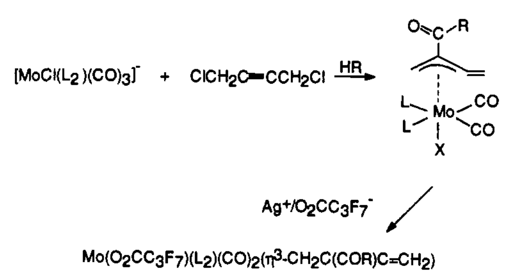
Scheme 13.



$L_nM = Mo(\eta\text{-}C_5H_5)(CO)_2$, R = OMe (54); $L_nM = Fe(\eta\text{-}C_5H_5)(CO)$, B = OMe (55), NHEt (56), NEt_2 (57).

Scheme 14.

Brisdon and co-workers[29] first reported the formation of η^3-butadienyl complexes from the reaction of the carbonylate anion $[Mo(bipy)Cl(CO)_3]^-$ (bipy, 2,2′-bipyridine) with 1,4-dichlorobut-2-yne in wet methanol. The presence of water was found to be essential in the clean formation of $MoCl(bipy)(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)$ (**60**), since under anhydrous conditions in MeOH/THF an η^3-allyl complex was formed. This reaction was developed into a general synthetic route

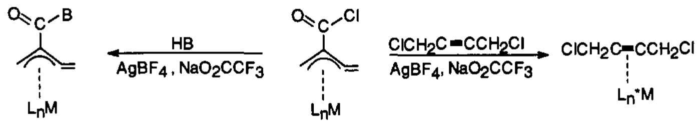


L_2 = bipy, X = Cl, R = OEt (61), NMe_2 (62), NEt_2 (63), NPr_2 (64), NHMe (65), NHEt (66), NHPr (67), $NHCH{=}CH_2$ (68), $NHCH_2C{\equiv}CH$ (69); L_2 = phen, R = NEt_2 (70); L_2 = bipy, X = $O_2CC_3F_7$, R = NHMe (71), NHEt (72), NHPr (73), NHPh (74).

Scheme 15.

(Scheme 15) for the preparation of a range of ester and amide substituted η^3-butadienyl complexes,[30–32] and by reacting halo-species with sodium perfluorocarboxylate salts in the presence of $AgBF_4$, soluble complexes amenable to X-ray crystallographic and NMR studies were obtained.

Although the mechanism of this reaction has not been established with certainty, it has been shown very recently[32] that in the complete absence of hydroxylic solvents this reaction affords a 1,2,3-η^3-butadienyl complex containing a reactive chlorocarbonyl functionality on the C_2 atom which can be transformed in high yields to other products. The complete butadienyl ligand is displaced on heating by an excess of alkyne in the presence of AgO_2CCF_3 to afford an alkyne complex (**82**) which is an analogue of others in the series Mo(η^2-alkyne)(CO)X_2L_2[33] (Scheme 16).



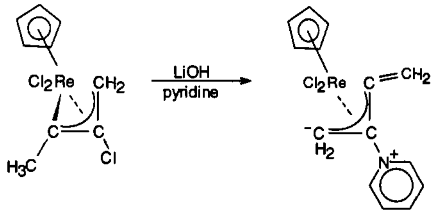
$L_nM = Mo(O_2CCF_3)(bipy)(CO)_2$, R = OMe (75), NHEt (76), NHCH(Me)Ph (77), OCOCF$_3$ (78); $L_nM = Mo(O_2CCF_3)(phen)(CO)_2$, B = OMe (79), NHEt (80), NHCH(Me)Ph (81); $L_n'M = Mo(O_2CCF_3)_2(phen)(CO)$ (82).

Scheme 16.

It is also interesting to note that analogues of the Pt^{II}-η^1-butadienyl complexes prepared by Green and co-workers from 1,3-butadienes,[10–12] were first prepared by Furlani *et al.*[34] in 1977 from the reaction of *cis*-$PtCl_2(PPh_3)_2$ and isopropenylacetylene in the presence of ethanol and hydrazine hydrate. Both *trans*-$PtCl(PPh_3)_2(C({=}CH_2)C(Me)C{=}CH_2)$ (**83**) and *trans*-$Pt(C_2C(Me){=}CH_2)(PPh_3)_2(C({=}CH_2)C(Me)C{=}CH_2)$ (**84**) were isolated, and the intermediacy of a Pt—H species was suggested *en route* to the final products.

3.5. *Miscellaneous methods*

An unusual zwitterionic butadienyl complex (**85**) has been characterized crystallography by Hermann and co-workers.[35] This complex was prepared by reacting $ReCl_2(\eta\text{-}C_5H_5)(\eta^1:\eta^3\text{-}C(Me)$

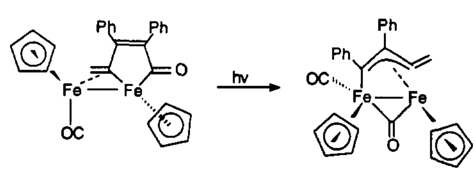


(85)

Scheme 17.

$C(Cl)CH_2)$ with LiOH and pyridine (Scheme 17) and has interesting structural features which are discussed in the next section.

Unlike allyl analogues, very few butadienyl complexes of di- or poly-nuclear metal centres are known at present. Casey and co-workers[36] isolated a dinuclear iron complex (**86**) formed by a

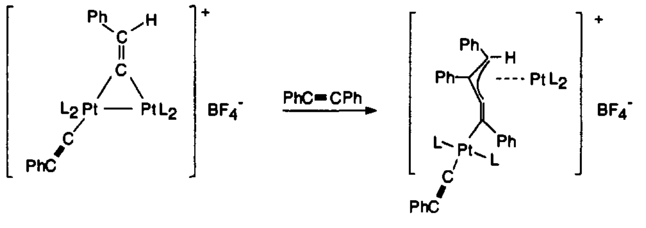


(86)

Scheme 18.

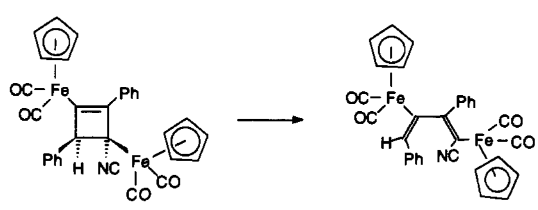
photolytically induced rearrangement of a metallocyclopentenone (Scheme 18), in which the M—M bond is retained.

By contrast, photochemical reaction of a diplatinum μ-alkenylidene complex with PhC≡CPh



Scheme 19.

occurs with C—C coupling but Pt—Pt scission to give the cationic diplatinum μ-$\eta^1:\eta^3$-butadienediyl complex (**87**) (Scheme 19) in good yield. The mechanism of formation of (**87**) remains undetermined, but ^{13}C labelling indicated that a complex rearrangement involving at least one branching point is probable.[37] A dimetal 2,4-disubstituted η^1-butadienyl system (**88**) resulting from thermolysis of a cyclobutenyldiiron complex Fe{C=C(Ph)C(CN)[Fe(CO)$_2$(η-C_5H_5)]CHPh}(η-C_5H_5)(CO)$_2$ (Scheme



(**88**)

Scheme 20.

20) has also been characterized by Struchkov and co-workers.[38] Although not mentioned in their paper, their structural studies indicate that the reaction proceeds via a conrotatory process as established by Bruce *et al.*[23] for a Ru substituted cyclobutenyl ring.

4. STRUCTURAL AND SPECTROSCOPIC PROPERTIES

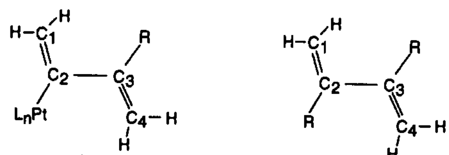
4.1. 2-η^1-*Butadienyl derivatives*

Although the structures of some dozen 2-η^1-butadienyl transition metal complexes have been published, almost half of these contain the Ru(η-C_5H_5)(L)$_2$ fragment bonded to a highly substituted butadienyl ligand, and of the remainder several contain incomplete or imprecise data. As so few L_nM fragments are represented, any subtle trends in the effect of the metal centres on the structural parameters of the organic moiety are difficult to discern, but in general the M—C_2 bond lengths for each metal M (Table 1) appear typical of those found for M—C(sp^2) σ-linkages. Of those complexes listed in Table 1 all but the Pt analogues can be described in terms of a *s-cis* conformation of the diene fragment, albeit with a varying degree of distortion, manifested mainly in terms of torsion angles C_1C_2—C_3C_4 of 55° and greater, rather than a widening of the C_1—C_2—C_3 or C_2—C_3—C_4 angles as noted for 1,4-substituted sterically hindered buta-1,3-dienes.[39] Thus, in complexes with a non-planar *s-cis* or orthogonal geometry, C_1—C_2 and C_2—C_3 distances are close to a normal C=C bond length, with the C_3—C_4 linkages averaging 1.48 Å. These values are also typical for 2,3-substituted orthogonal buta-1,3-dienes containing bulky organic groups.[40]

The structures of the two Pt analogues are significantly different from the others. In both complexes of known structure, (**14**) and (**83**), the butadienyl ligand adopts a virtually planar *s-trans* conformation with the C_4 skeleton orthogonal to the approximately square planar coordination geometry around Pt, which permits a minimization of the steric interactions (Scheme 21). However, the most interesting feature is the bond lengths within this ligand. As shown in Table 1, despite the larger than desirable uncertainties in the internuclear distances, there appears to be a shortening of the central C—C bond at the expense of the C_1—C_2 linkage. This is atypical of *s-trans* butadiene or

Table 1. Structural parameters of the 2-η^1-butadienyl ligands in $L_nM\{C_2({=}C_1R_1R_2)C_3(R_3){=}C_4R_4R_5\}$

L_nM	Compound	M—C_2 (Å)	$C_1{=}C_2$ (Å)	C_2—C_3 (Å)	$C_3{=}C_4$ (Å)	C_1—C_2—C_3 angle (°)	C_2—C_3—C_4 angle (°)	Torsion angle (°)	Ref.
$Re(CO)_5$	**2**	2.25(3)	1.37(3)	1.52(3)	1.29(4)	—	—	83	4
$Fe(\eta\text{-}C_5H_5)(CO)_2$	**88**	2.035(3)	1.345(4)	1.483(4)	1.334(4)	124.5(3)	122.7(2)	88.4	36
$Ru(\eta\text{-}C_5H_5)(CO)(PPh_3)$	**37**	2.100(5)	1.367(7)	1.480(7)	1.356(7)	113.5(4)	125.1(4)	73.1	21
$Ru(\eta\text{-}C_5H_5)(CO)(PPh_3)$	**44**	2.109(6)	1.363(8)	1.467(8)	1.346(9)	118.8(6)	127.5(6)	97.2	22
$Ru(\eta\text{-}C_5H_5)(CO)(PPh_3)$	**40**	2.106(5)	1.362(8)	1.493(8)	1.328(8)	113.2(5)	126.5(5)	81.0	21
$Ru(\eta\text{-}C_5H_5)(dppe)$	**46**	2.068(4)	1.370(6)	1.484(6)	1.346(6)	114.4(4)	124.3(4)	80.6	19
$Ru(\eta\text{-}C_5H_5)(PPh_3)(CNBu)$	**47**	2.074(3)	1.382(5)	1.478(4)	1.362(4)	112.8(3)	117.9(3)	105	16
$Co(Bupy)(dmg)_2$	**6**	1.954(15)	1.341(23)	1.454(22)	1.304(29)	118.4(15)	124.3(17)	54	7
$Co(Me_2py)(dmg)_2$	**8**	2.002(10)	1.330(16)	1.415(17)	1.292(23)	120.6(10)	128.7(15)	63	9
$Pt(PPh_3)_2\{C_2C(Me){=}CH_2\}$	**83**	2.09(2)	1.48(3)	1.42(3)	1.34(4)	124(2)	122(2)	0	32
$PtCl(PPh_3)_2$	**14**	2.08(3)	1.55(4)	1.27(4)	1.27(4)	123(3)	120(3)	5.8	7



(A) (B)

(83), $C_1C_2 = 1.48(3)$, $C_3C_4 = 1.34(4)$, $C_2C_3 = 1.42(3)$; (14), $C_1C_2 = 1.55(4)$, $C_3C_4 = 1.27(4)$, $C_2C_3 = 1.27(4)$ A.

R = H, $C_1C_2 = C_3C_4 = 1.344(1)$, $C_2C_3 = 1.467(3)$; R = Me, $C_1C_2 = C_3C_4 = 1.349(6)$, $C_2C_3 = 1.504(5)$ A.

Scheme 21.

other planar 2,3-disubstituted derivatives such as 2,3-dimethylbuta-1,3-diene,[41] and it remains to be seen whether this is a genuine electronic effect.

4.2. 1,2,3-η^3-*Butadienyl complexes*

The structural parameters for the π-η^3-butadienyl complexes which have been described in this review and have been characterized crystallographically are tabulated in Table 2. All complexes exhibit some similar features despite the large variation of ligand substituents and metal centres. Thus, for all mononuclear complexes the transoid butadienyl fragment consists of an allyl moiety bound somewhat asymmetrically to the metal via all three carbon atoms, with the *exo*-C=CR$_2$ unit bent away from the metal and out of the C_1—C_2—C_3 plane giving non-bonding M—C_4 distances. As in η^3-allyl complexes of the same or similar metal/auxillary ligand systems, the central carbon atom of the allylic fragment lies closer (or for **20** equidistant) to the metal atom than does the terminal carbon atom C_1, and C_1—C_2 and C_2—C_3 separations, as well as C_1—C_2—C_3 angles are in most complexes within the range of values typical for coordinated η^3-allyl ligands. In all structures C_3 is bonded to the metal via a shorter bond than C_1, which is indicative of some multiple bond character in the M—C_3 linkage. These net effects are evident in the ^{13}C NMR data which are summarized for a selection of complexes in Table 3, and show a pronounced low field shift for C_3 in all examples. In view of these observations, it has been suggested[22] that a degree of carbenoid character may be present in the M—C_3 bond, indicating a contribution from a zwitterionic form (A) (Scheme 22) in complexes which carry electron-withdrawing —CN or —CF_3 substituents, which serve to deshield even further the quaternary carbon C_3.

Based on a consideration of the structures of the Pt derivatives (**20**) and (**26**) and comparison with bond lengths in the uncoordinated C=CH_2 bond of ligated allene complexes and in buta-1,3-diene itself, contributions from localized Pt—C(3) bonding (B), and from formalism (C) (Scheme 23) have also been suggested.[12]

Despite the unusual synthetic route to the Re complex (**85**), which involves abstraction of HCl from a Re^{V} allylidene complex and introduction onto C_2 of pyridine (see Scheme 17), neither its structural properties nor its ^{13}C NMR data are greatly atypical of others in Tables 2 or 3. By comparison with the structure of Re(η-C_5H_5)Br_2(η^3-C_3H_5)[42] the C—C separations in the allyl fragment of the butadienyl ligand are very slightly longer, whereas the Re—C_1 and the Re—C_3 separations are shorter by 0.05 and 0.15 Å, respectively, than the analogous distances in the Re allyl complex. The zwitterionic nature of the pyridine-containing C_4 ligand has been assessed[35] in terms of forms (A) and (B) in Scheme 24.

The presence of a bridging butadienyl ligand in the dinuclear iron complex (**86**) is based solely on spectroscopic data,[36] but a μ-η^1 : η^3-butadienyl ligand bridging between two separate Pt centres was established for (**87**) by Lukehart and co-workers[37] using X-ray crystallography. The structure of (**87**) is depicted in Scheme 19, and the cation consists formally of two organometallic moieties, viz [Pt(L)$_2$(η^3-allyl)]$^+$ and neutral *trans*-Pt(L)$_2$(C≡CPh)(η^1-alkenyl) fragments, each of which exhibits the expected structural features. Substitution at C_4 by the σ-bonded Pt fragment does not perturb the C_1=C_2 double bond, and angles around the *exo*-alkylidene carbon of 120(1), 116(1) and 123(1)° indicate a planar arrangement and approximate sp^2 hybridization of this atom.

Table 2. Structural data for 1,2,3-η^3-butadienyl complexes[a]

ML_n	Compound	R_1	R_2	R_3	R_4	R_5	M—C_1 (Å)	M—C_2 (Å)	M—C_3 (Å)	C_1—C_2 (Å)	C_2—C_3 (Å)	C_3—C_4 (Å)	C_1—C_2—C_3 (°)	C_2—C_3—C_4 (°)	Ref.
Mo(η-C_5Me_5)$(CO)_2$	**24**	H	H	H	H	H	2.328(15)	2.208(14)	2.198(15)	1.348(22)	1.391(20)	1.353(24)	120(1)	139(1)	14
Mo($O_2CC_3F_7$)$(CO)_2$(bipy)	**71**	H	H	CONHMe	H	H	2.314(13)	2.235(10)	2.200(10)	1.416(17)	1.399(18)	1.335(18)	112.5(10)	141.7(10)	31
W(η-C_5H_5)$(CO)_2$	**42**	CN	CN	Ph	CN	CN	2.285(8)	2.253(7)	2.075(8)	1.480(9)	1.439(9)	1.355(10)	104.5(6)	132.1(7)	19
Re(η-C_5H_5)Cl_2	**85**	H	H	py	H	H	2.190(6)	2.116(6)	2.046(7)	1.445(9)	1.428(8)	1.337(9)	113.0(6)	134.1(7)	35
Fe(η-C_5H_5)(PPh_3)	**4**	F	F	CF_3	CF_3	CF_3	1.969(7)	1.981(7)	1.905(6)	1.426(9)	1.442(8)	1.319(8)	—	134.5(7)	4
Ru(η-C_5H_5)(PPh_3)	**43**	CF_3	CF_3	Ph	CN	CN	2.202(7)	2.138(7)	1.997(7)	1.46(1)	1.42(1)	1.37(1)	113.5(6)	131.4(7)	22
Ru(η-C_5H_5)(PPh_3)	**50**	CO_2Me	H	CO_2Me	Ph	H	2.190(5)	2.108(6)	2.061(6)	1.432(8)	1.431(8)	1.335(8)	116.6(5)	141.8(6)	24
Ru(η-C_5H_5)(PPh_3)	**49**	CN	CN	Ph	CN	CN	2.231(4)	2.135(4)	1.919(5)	1.476(6)	1.432(7)	1.383(6)	—	—	17
Ru(η-C_5H_5)(CO)	**45**	CO_2Me	H	Ph	CO_2Me	CN	2.218(4)	2.160(4)	2.047(4)	1.431(5)	1.422(5)	1.344(5)	114.2(3)	136.5(4)	23
Co(PPh_3)$(CO)_2$	**23**	H	H	H	Me	Me	2.119(4)	2.015(4)	1.986(4)	1.305(6)	1.387(7)	1.406(6)	116.0(4)	146.3(4)	8
Pt$(PPh_3)_2$	**26**	Ph	H	Ph	H	H	2.291(14)	2.201(14)	2.075(13)	1.40(2)	1.46(2)	1.31(2)	115(1)	140(1)	16
Pt$(PPh_3)_2$	**20**	H	H	Et	H	H	2.20(2)	2.20(2)	2.09(2)	1.42(3)	1.44(3)	1.26(4)	117(2)	141(2)	12

[a] Butadienyl labelling scheme for Tables 2 and 3.

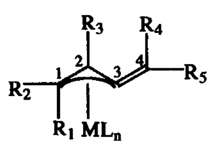
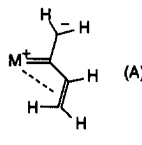
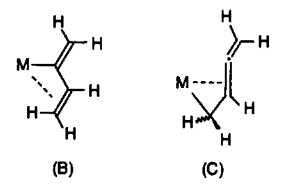


Table 3. ^{13}C NMR data for 1,2,3-η^3-butadienyl complexes

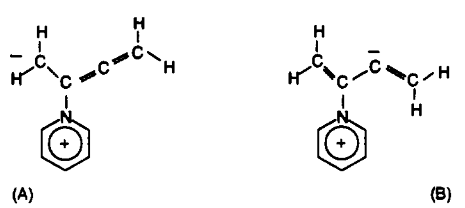
Compound	C_1	C_2	C_3	C_4	Ref.
71	52.6	—	166.3	106.1	31
24	44.6	53.0	174.8	102.6	14
42	79.4	4.7	206.6	—	19
85	26.6	83.6	160.6	101.3	35
49	85.1	7.3	218.8	66.7	20
16	75.9	97.0	168.6	99.6	11
20	74.1	120.8	167.2	99.7	12



Scheme 22.



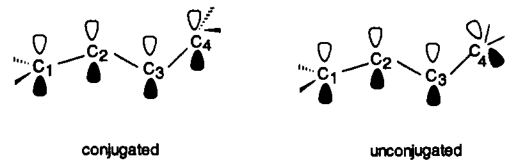
Scheme 23.



Scheme 24.

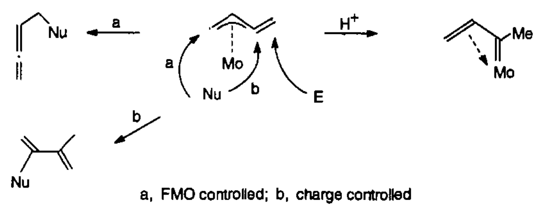
5. THEORETICAL DESCRIPTION OF BONDING, AND REACTIVITY STUDIES OF 1,2,3-η^3-BUTADIENYL COMPLEXES

Of major interest in the development of the chemistry of the 1,2,3-η^3-butadienyl ligand is a theoretical description of its bonding and reactivity. The first such study was published in 1991[32] and employed standard EHMO methods applied to a model of the structure of $Mo(O_2CC_3F_7)(CO)_2$ (bipy)(η^3-$CH_2C(CONHMe)C{=}CH_2$) (**71**), for which the positions of the H atoms on the C_4 skeleton were unknown. In the first stage of the analysis, the degree of interaction between the terminal $C{=}CH_2$ moiety and the allyl fragment was explored, which at the extremes will permit conjugation or minimize it (Scheme 25).



Scheme 25.

Preference for the unconjugated π-system was found, and when the arrangement of C_4 relative to the $C_1C_2C_3$ plane that yielded the lowest energy was established, a fragment MO analysis was carried out for the η^3-butadienyl and the d^4 MoL_5 moieties. It was shown that when the two fragments interact the π and π^* components of the double bond of the *exo*-C=CH$_2$ unit of the butadienyl system remain largely unchanged in energy and play no significant role in the binding of the two fragments. Consequently it was expected that this double bond will react in an independent sense towards nucleophiles and electrophiles. Furthermore, within the η^3-allyl fragment nucleophillic attack, if FMO controlled, would be expected at C_1, the position with the larger atomic coefficient

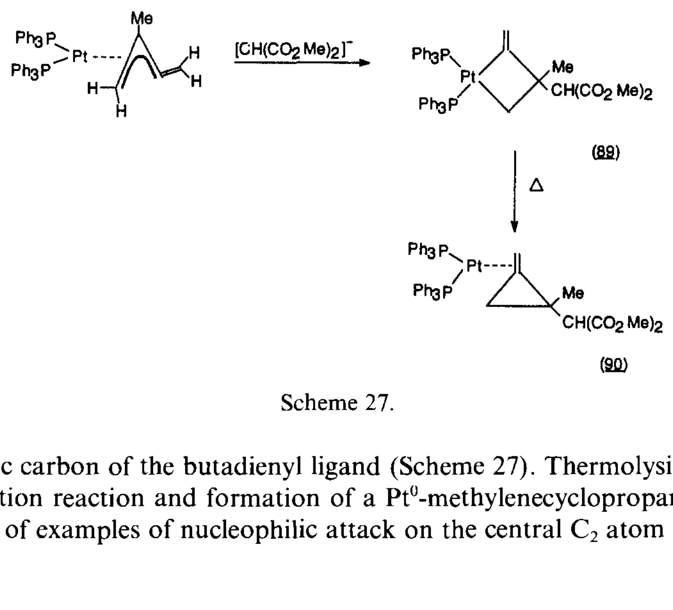


Scheme 26.

in the LUMO and the least steric hindrance. This would yield an allene (Scheme 26). In contrast, the charge distribution in the η^3-butadienyl ligand would direct nucleophilic attack towards C_3, to yield a 1,3-butadiene. In keeping with these arguments, the reaction of $NHEt_2$ with Mo(η-C_5H_5)$(CO)_2$(η^3-CH$_2$C(CONEt$_2$)C=C(Me)(Ph)), containing the Mo(η-C_5H_5)$(CO)_2$ fragment which is isoelectronic with Mo($O_2CC_3F_7$)(bipy)$(CO)_2$ but with slightly differing frontier orbital energies,[43] yields Mo(η-C_5H_5)$(CO)_2$(C(CONEt$_2$)(CH=C(Me)Ph)CH$_2$NEt$_2$).[28] Electrophilic attack, if charge controlled, is predicted at C_4, and later Green and co-workers[14] showed that protonation of Mo(η-C_5Me_5)$(CO)_2$(η^3-CH$_2$CHC=CH$_2$) (**24**) using triflic acid yields an η^4-vinylketene complex, Mo(η-C_5Me_5)(OSO_2CF_3){η^4-CH$_2$=CHC(Me)=C=O}(CO), probably via an η^3-vinylcarbene intermediate formed by protonation of the butadienyl ligand at C_4, and followed by intramolecular insertion of CO.

In the course of the MO analysis the reason why complex (**71**) does not show a significant "nose-up" tilt typical of the η^3-bonded allyl group was rationalized, and a subsequent X-ray analysis of (**24**), in which hydrogen atoms were located,[14] confirmed the earlier theoretical analysis which predicted that the pair of H atoms on C_1 should lie orthogonal to the pair on C_4.

Few other studies on either the reactivity or theoretical bonding description of η^3-butadienyl complexes of other metals have appeared in the literature, but in one communication[11] evidence is provided that the cations in [Pt(PPh$_3$)$_2${η^3-CH$_2$C(R)C=CH$_2$}]PF$_6$ [R = H (**16**) or Me (**18**)] are highly reactive and do not mimic the reactions of [Pt(PPh$_3$)$_2$(η^3-allyl)]$^+$ cations. Thus, reaction of (**18**) with the soft carbon nucleophile K[CH(CO$_2$Me)$_2$] under mild conditions yielded an air-stable *exo*-2-methyleneplatinacyclobutane derivative (**89**), produced by selective attack of the carbanion



Scheme 27.

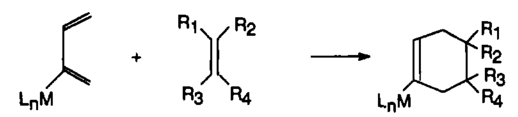
on the central allylic carbon of the butadienyl ligand (Scheme 27). Thermolysis of (**89**) resulted in a reductive elimination reaction and formation of a Pt^0-methylenecyclopropane complex (**90**). In view of the paucity of examples of nucleophilic attack on the central C_2 atom of an allyl ligand in

Pt^{II} or Pd^{II} chemistry,[44] these observations have significance in both a synthetic and theoretical context.

6. INTERMEDIATES IN ORGANIC SYNTHESIS

Synthetic applications in organic chemistry of both η^1- and η^3-allyl complexes are legion,[45] and encompass many reactions in which the exact identity of the reactive metal–enyl intermediate is in many cases not well defined. Both η^1-butadienyl and η^3-butadienyl complexes possess appropriate structural and bonding features which should enable them to participate in many analogous reactions, although their chemistry remains largely unexplored in this context. In the final section of this review we concentrate on reactions which differ from those of η^1- and η^3-allyls, and/or which illustrate important reactivity patterns of the butadienyl ligand which are of actual or potential use in synthesis.

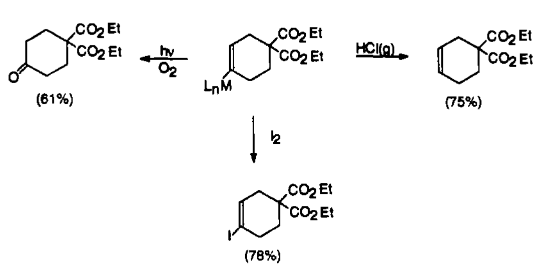
Although there has been considerable interest in the organic applications of cycloaddition reactions between transition metal complexes containing σ-bonds to unsaturated ligands,[46] and in using activated 2-substituted alkadienes, such as Danishefsky's diene, to facilitate [4+2] cycloadditions, we are aware of very few publications in which preformed 2-transition-metal-substituted 1,3-butadienes have been used in this most important method of generating new C—C bonds. The pioneering study by Giering and co-workers in 1985,[47] in which they demonstrated the reactivity of $Fe(\eta\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C({=}CH_2)CH{=}CH_2)$ (**5**) towards electrophilic dienophiles as a route to more than a dozen cyclohexene, cyclohexadiene, iminolactone, and δ-lactam derivatives was not followed up until 7 years later when first Tada and Shimizu,[13] and then Welker and co-workers,[7,9] used cobalt bis(dimethylglyoxime)–1,3-butadiene complexes to carry out cycloaddition reactions (Scheme 28).



L_nM = $Co(dmg)_2(py)$ (**7**), dienophile = dimethyl and diethyl acetylenedicarboxylate, maleic anhydride, benzoquinone, dimethyl-fumarate, -maleate, -methylenemalonate, methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, methyl vinyl ketone, N-phenylmaleimide; L_nM = $Co(dmg)_2(pyBu^t)$ (**6**), dienophile = diethyl methylenemalonate.

Scheme 28.

All three groups of workers have commented on the very reactive nature of the 2-transition metal substituted buta-1,3-diene compared to a trialkyl- or trialkoxysilyl-substituted analogue, and Tada and Shimizu[13] have proposed that backdonation from filled Co $d(\pi)$ orbitals to π^*(butadiene) may be instrumental in promoting the activity. In a very detailed study Welker and co-workers[9] have demonstrated using X-ray crystallography that the butadienyl ligands in (**6**) and (**8**) do adopt the *s-cisoid* conformation needed to facilitate Diels–Alder reactions under mild conditions, and they also developed methods for the cleavage of the Co—C bonds in cycloadducts which would yield organic products (Scheme 29) as well as a Co derivative which could be recycled.

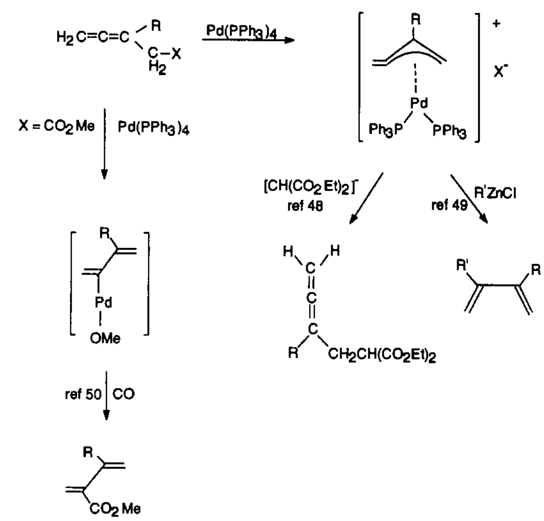


L_nM = $Co(py)(dmg)_2$

Scheme 29.

Demetalation reactions which maintain the sterochemical integrity found in the metallo-cycloadducts were also determined. This is an important feature for the future exploitation of these reagents, in view of the high preference for *exo*-selective Diels–Alder reactions to occur, so providing access to relative stereochemistries previously difficult to obtain.

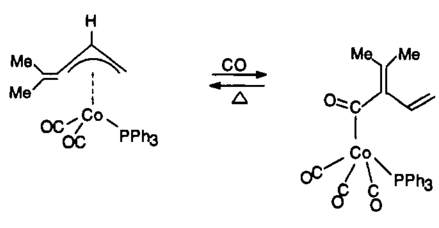
There are several reports of the intermediacy of η^1- or η^3-butadienylpalladium(II) species in palladium catalysed reactions of allenes of the type $H_2C{=}C{=}C(R)CH_2X$ (X = OR, OCOR or OSO_2R), or their alkyl substituted derivatives,[48–50] but to date none of the proposed intermediates



Scheme 30.

have been substantiated spectroscopically (Scheme 30). Gore and co-workers[48] showed that soft carbonucleophiles yield allenes, whereas Vermeer and co-workers[49] demonstrated that hard nucleophiles such as alkylzinc or alkylmagnesium salts afford 1,3-dienes. In terms of the η^3-butadienyl–Pd complex proposed as an intermediate, this would signify attack at C_1 and C_3 respectively, which are the two positions shown by theoretical calculations of $MoCl(CO)_2(bipy)(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)$[31] (which are not of course necessarily valid for cationic Pt or Pd complexes) to be susceptible to nucleophilic attack. However, as noted earlier, the soft nucleophile $[CH(CO_2Me)_2]^-$ reacts at C_2 in the Pt analogue $[Pt(PPh_3)_2(\eta^3\text{-}CH_2C(Me)C{=}CH_2)]^+$ to form an *exo*-2-methyleneplatenacyclobutane derivative[11] (Scheme 27), and hence there would appear considerable scope for both further theoretical studies and for practical assessments of the role of steric and electronic control in catalytic processes involving η^3-butadienyl intermediates.

Finally in terms of the carbonylation reaction in Scheme 30, which generates regioselectivity 1,3-diene-2-carboxylates, it is interesting to note a close parallel with the reversible reaction between



(91)

Scheme 31.

CO and $Co(PPh_3)(CO)_2(\eta^3\text{-}CH_2CHC{=}CMe_2)$ (**23**) by Welker and co-workers[8] (Scheme 31), which yields an acyl derivative (**91**), presumably via CO insertion into the Co—C bond of an intermediate η^1-butadienyl complex.

7. CONCLUSIONS

Synthetic routes to 2-η^1- and/or 1,2,3-η^3-butadienyl derivatives of some ten transition metals are now available. Several are general procedures which are capable of providing access to a far wider range of complexes than has been reported to date. Structurally the η^3-butadienyl complexes of different transition metals exhibit similar features despite the considerable variation in ligand substituents and metal coordination geometries. Although the limited, theoretical treatments which are currently available indicate bonding similarities between the η^3-allyl ligand and the η^3-bonded fragment of the butadienyl ligand, significant differences in reactivities of analogues containing these ligands have already been noted. Interconversion between η^3- and η^1-bonding modes of the butadienyl ligand is readily achievable in many instances. Structural variations in L_nM–2-η^1-butadienyl complexes have been noted, and the high reactivity of iron and cobalt derivatives has been exploited in a range of cycloaddition reactions. The butadienyl ligand provides an interesting example of a ligand which offers a multiplicity of coordination modes. It is apparent from recent studies that both classes of butadienyl complexes highlighted in this review will feature significantly in the further development of C_4 organometallic chemistry.

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REFERENCES

1. B. M. Trost and R. C. Bunt, *J. Am. Chem. Soc.* 1994, **116**, 4089; A. Togni, C. Breutal, A. Schnyder, F. Spindler, H. Laudert and A. Tijani, *J. Am. Chem. Soc.* 1994 **116**, 4062; J. Kang, W. O. Cho and H. G. Cho, *Tetrahedron: Asymmetry* 1994, **5**, 1347; M. Sawamura, H. Nagata, H. Sakamoto and Y. Ito, *J. Am. Chem. Soc.* 1992, **114**, 2586; G. Consiglio and R. Waymouth, *Chem. Rev.* 1989, **89**, 257; C. G. Frost, J. Howarth and J. M. J. Williams, *Tetrahedron: Asymmetry* 1992, **3**, 1089; B. M. Trost, D. L. Van Vranken and C. Bingel, *J. Am. Chem. Soc.* 1992, **114**, 9327.
2. P. S. Pregosin, H. Rüegger, R. Salzmann, A. Albinati, F. Lianza and R. W. Kunz, *Organometallics* 1994, **13**, 83; P. D. Hampton, S. Wu, T. M. Alam and J. P. Claverie, *Organometallics* 1994, **13**, 2066; R. H. Yu, S. McCallum and L. S. Liebeskind, *Organometallics* 1994, **13**, 1476; Y. I. M. Nilsson, P. G. Andersson and J. E. Bäckvall, *J. Am. Chem. Soc.* 1993, **115**, 6609.
3. A. N. Nesmeyanov, N. E. Kolobova, I. B. Zlotina, B. A. Lokshin, I. F. Leshcheva, G. K. Knobina and K. N. Anisimov, *J. Organomet. Chem.* 1976, **110**, 339.
4. A. N. Nesmeyanov, G. G. Aleksandrov, N. G. Bokii, I. B. Zlotina, Yu. T. Struchkov and N. E. Kolobova, *J. Organomet. Chem.* 1976, **111**, C9.
5. T. A. Bauch and W. P. Griering, *J. Organomet. Chem.* 1976, **114**, 165.
6. B. J. Brisdon, D. A. Edwards and J. W. White, *J. Organomet. Chem.* 1979, **175**, 113.
7. T. L. Smalley Jr, M. W. Wright, S. A. Garman, M. E. Welker and A. L. Rheingold, *Organometallics* 1993, **12**, 998.
8. H. L. Stokes, T. L. Smalley Jr, M. L. Hunter and M. E. Welker, *Inorg. Chim. Acta* 1994, **220**, 305.
9. M. W. Wright, T. L. Smalley Jr, M. E. Welker and A. L. Rheingold, *J. Am. Chem. Soc.* 1994, **116**, 6777.
10. S. A. Benyunes, M. Green, M. McPartin and C. B. M. Nation, *J. Chem. Soc., Chem. Commun.* 1989, 1887.
11. S. A. Benyunes, L. Brandt, M. Green and A. W. Parkin, *Organometallics* 1991, **10**, 57.
12. S. A. Benyunes, L. Brandt, A. Fries, M. Green, M. F. Mahon and T. M. T. Papworth, *J. Chem. Soc., Dalton Trans.* 1993, 3585.
13. M. Tada and T. Shimizu, *Bull. Chem. Soc. Jpn* 1992, **65**, 1252.
14. S. A. Benyunes, R. J. Deeth, A. Fries, M. Green, M. McPartlin and C. B. M. Nation, *J. Chem. Soc., Dalton Trans.* 1992, 3453.
15. C. B. M. Nation, Ph.D. Thesis, University of London (1991).
16. R. P. Hughes, J. J. J. Lambert and A. L. Rheingold, *Organometallics* 1985, **4**, 2055.
17. M. I. Bruce, J. R. Rodgers, M. R. Snow and A. G. Swincer, *J. Chem. Soc., Chem. Commun.* 1981, 271.
18. M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *J. Organomet. Chem.* 1982, **226**, C1.
19. M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics* 1985, **4**, 494.
20. M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics* 1985, **4**, 501.
21. M. I. Bruce, M. J. Liddell, M. R. Snow and E. R. T. Tiekink, *Organometallics* 1988, **7**, 343.
22. M. I. Bruce, T. W. Hambley, M. J. Liddell, M. R. Snow, A. G. Swincer and E. R. T. Tiekink, *Organometalllics* 1990, **9**, 96.

23. M. I. Bruce, D. N. Duffy, M. J. Liddell and E. R. T. Tiekink, *Organometallics* 1992, **11**, 1527.
24. M. I. Bruce, A. Catlow, M. P. Cifuentes, M. R. Snow and E. R. T. Tiekink, *J. Organomet. Chem.* 1990, **397**, 187.
25. A. C. Dema, C. M. Lukehart, A. T. McPhail and D. R. McPhail, *J. Am. Chem. Soc.* 1989, **111**, 7615.
26. A. C. Dema and C. M. Lukehart, *Organometallics* 1993, **12**, 583.
27. F. Giuliéri and J. Benaim, *Nouv. J. Chim.* 1985, **9**, 335.
28. F. Giuliéri and J. Benaim, *J. Organomet. Chem.* 1984, **276**, 367.
29. M. G. B. Drew, B. J. Brisdon, D. W. Brown and C. R. Willis, *J. Chem. Soc., Chem. Commun.* 1986, 1510.
30. B. J. Brisdon, A. G. W. Hodson, M. F. Mahon and K. C. Molloy, *J. Organomet. Chem.* 1988, **344**, C8.
31. B. J. Brisdon, R. J. Deeth, A. G. W. Hodson, C. M. Kemp, M. F. Mahon and K. C. Molloy, *Organometallics* 1991, **10**, 1107.
32. B. J. Brisdon, A. G. W. Hodson and M. F. Mahon, *Organometallics* 1994, **13**, 2566.
33. B. J. Brisdon, A. G. W. Hodson, M. F. Mahon, K. C. Molloy and R. A. Walton, *Inorg. Chem.* 1990, **29**, 2701.
34. A. Furlani, M. V. Russo, A. C. Villa, A. G. Manfredotti and C. Guastini, *J. Chem. Soc., Dalton Trans.* 1977, 2154.
35. R. A. Fischer, R. W. Fischer, W. A. Hermann and E. Herdtweck, *Chem. Ber.* 1989, **122**, 2035.
36. C. P. Casey, W. H. Miles, P. J. Fagan and K. J. Haller, *Organometallics* 1985, **4**, 559.
37. E. Baralt, C. M. Lukehart, A. T. McPhail and D. R. McPhail, *Organometallics* 1991, **10**, 516.
38. N. E. Kolobova, T. V. Rozantseva, Yu. T. Struchkov, A. S. Batsanov and A. S. Bakhmutov, *J. Organomet. Chem.* 1985, **292**, 247.
39. H. Hopf, R. Hänel, P. G. Jones and P. Bubenitschek, *Angew. Chem., Int. Ed. Engl.* 1994, **33**, 1369.
40. H. Hopf, M. Traetteberg and H. Lipka, *Angew. Chem., Int. Ed. Engl.* 1994, **33**, 204.
41. C. F. Aten, L. Hedberg and K. Hedberg, *J. Am. Chem. Soc.* 1968, **90**, 2463.
42. W. A. Hermann, M. Flöel and E. Herdtwek, *J. Organomet. Chem.* 1988, **358**, 321.
43. B. J. Brisdon and R. J. Deeth, unpublished observations.
44. B. Tjaden and J. M. Stryker, *J. Am. Chem. Soc.* 1990, **112**, 6420; D. Curtis and O. Eisenstein, *Organometallics* 1984, **3**, 887; R. A. Periani and R. G. Bergman, *J. Am. Chem. Soc.* 1984, **106**, 7272; M. Ephritikhine, B. R. Francis, M. L. H. Green, R. E. MacKenzie and M. J. Smith, *J. Chem. Soc., Dalton Trans.* 1977, 1131.
45. Y. Yamamoto and N. Asao, *Chem. Rev.* 1993, **93**, 2207; S. A. Godleski, in *Comprehensive Organic Syntheses* (Edited by B. M. Trost), Vol. 3, pp. 585–661. Pergamon, New York (1991); D. C. Billington, *Comprehensive Organic Syntheses* (Edited by B. M. Trost), Vol. 3, pp. 423–434. Pergamon, New York (1991) and references therein.
46. D. M. T. Chan, in *Comprehensive Organic Syntheses* (Edited by B. M. Trost), Vol. 5, pp. 271–314. Pergamon, New York (1991); A. Wojcicki, *Coord. Chem. Rev.* 1990, **105**, 35; M. Rosenblum, *J. Organomet. Chem.* 1986, **300**, 191; M. E. Welker, *Chem. Rev.* 1992, **92**, 97.
47. P. W. Waterman, J. E. Belmonte, T. E. Bauch, P. A. Belmonte and W. P. Giering, *J. Organomet. Chem.* 1985, **294**, 235.
48. D. Djahanbini, B. Cazes and J. Gore, *Tetrahedron Lett.* 1984, **25**, 203.
49. H. Kleijn, H. Westmijze, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas* 1983, **102**, 378.
50. J. Nokami, A. Maihara and J. Tsuji, *Tetrahedron Lett.* 1990, **31**, 5629.