Some reactions of transition metal complexes containing unsaturated ligands with M—C(sp) or M—C(sp²) bonds
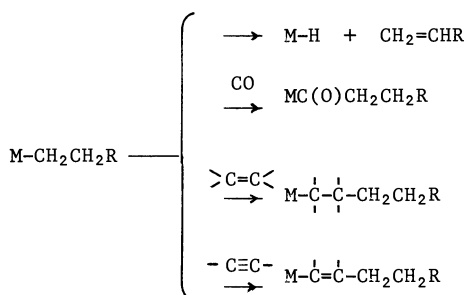
Michael I. Bruce

Jordan Laboratories, Department of Physical and Inorganic Chemistry,
University of Adelaide, Adelaide, South Australia 5001

Abstract – Compounds with M-C(sp²) or M-C(sp) bonds show a reactivity
different from that of metal-alkyl complexes. This paper describes some
reactions of transition metal acetylides, which are characterised by
electrophilic additions to the β-carbon. Cycloaddition to olefins has
given cyclobutenyl, butadienyl and allylic derivatives, while reactions
with tropylium and arenediazonium salts generate new types of vinylidene
complex. Unusual halogen-substituted vinylidene ligands are formed by
direct addition of Cl_2, Br_2 or I_2 to metal acetylides. Subsequent
reactions of these complexes are discussed. The conversion of cluster-
bound acetylides to vinylidenes is described, and the mild reduction of an
acetylide to carbon and methyl on an open Ru_5 cluster is an interesting
example of the modification of reaction pathways of small molecules by
metal clusters.

INTRODUCTION

The chemistry of metal-alkyl complexes, that is, those containing M-C(sp³) bonds,
is characterised by a pattern of reactivity which includes elimination and
insertion reactions:

$$M-CH_2CH_2R \begin{cases} \longrightarrow & M-H + CH_2=CHR \\ \xrightarrow{CO} & MC(O)CH_2CH_2R \\ \xrightarrow{>C=C<} & M-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CH_2CH_2R \\ \xrightarrow{-C\equiv C-} & M-\overset{|}{C}=\overset{|}{C}-CH_2CH_2R \end{cases}$$

However, there are few well established examples of insertion reactions occurring with
complexes containing M-C(sp) or M-C(sp²) bonds, although there is no shortage of such
complexes to study. Thus insertion of CO into the Fe-Ph bond on treatment of $FePh(CO)_2$-
$(\eta-C_5H_5)$ with PPh_3 has been described (1), while more recently the insertion of ethylene
into the Ru-Ph bond of $RuPh(PPh_3)_2(\eta-C_5H_5)$ has been studied; the products undergo β-H
elimination (2). Sen (3) has found an elegant synthesis of CO-C_2H_4 copolymers by
sequential insertion of CO and C_2H_4 into cationic palladium complexes; in alcohols, poly-
ketoesters were formed. Many years ago, the reaction between $Ru\{C(CO_2Me)=CH(CO_2Me)\}$-
$(PPh_3)_2(\eta-C_5H_5)$ and $C_2(CF_3)_2$ was found to proceed by attack of the vinyl on the alkyne,
giving a product with opposite configuration to that expected from a conventional insertion
reaction into the Ru-C bond (4). The reactions between $C_2(CO_2Me)_2$ and trans-$PdX(C_2R)(PR'_3)_2$
afforded trans-$PdX\{C(CO_2Me)=C(CO_2Me)(C_2R)\}(PR'_3)$ (R = Et, Bu, Ph; R' = Et, Bu; X = Cl, Br, I),
but for X = H, the alkyne inserts into the Pd-H bond instead (5).

Structural studies of a series of ruthenium complexes containing bonds from the metal to
variously hybridised carbon atoms (Table 1) show that the M-C(sp) bond length in acetylides
is close to that expected for a single bond, and contrasts markedly with those found for
carbonyl, carbene and vinylidene ligands. Thus, in spite of the formal isoelectronic
analogy between CO and RC_2^-, there seems to be little, if any, back-bonding from the metal
into the acetylide ligand. A theoretical study of electron distribution in the metal-
acetylide system confirms this feature and also points to a build-up of electron density
on the β-carbon atom (6).

TABLE 1. Ru–C Bond Distances in Several Complexes $Ru(C_R)(L)_2(\eta-C_5H_5)$

C_R	L_2	M–C (Å)	Reference
$C(OPr^i)=CHPh$	$(CO)(PPh_3)$	2.103(6)	a
cis-$C(CO_2Me)=CH(CO_2Me)$	(dppe)	2.071(12)	b
trans-$C(CO_2Me)=CH(CO_2Me)$	$(CO)(PPh_3)$	2.080(8)	b
$C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)$	$(PPh_3)_2$	2.082(5)	c
$C\{=C(CN)_2\}CPh=C(CN)_2$	$(CNBu^t)(PPh_3)$	2.074(3)	d
"	(dppe)	2.068(3)	e
$C\equiv CPh$	$(PPh_3)_2$	2.016(3)	f,g
"	(dppe)	2.009(3)	g
$C\equiv CPh$	$(PPh_3)_2$	2.017(9)	h
$\mid$			
CuCl			
C(OMe)Et	$(PPh_3)_2$	1.959(6)	i
CO	$(PPh_3)_2$	1.869(2)	f
$C=CMe_2$	$(PMe_3)_2$	1.845(7)	j
$C=CMePh$	$(PPh_3)_2$	1.863(10)	k
$C=CPh(C_7H_7)$	(dppe)	1.847(11)	l
$C=CPh(N=NC_6H_3Me_2-3,4)$	$(PPh_3)_2$	1.823(9)	m
$C=CBr(C_6H_4Br-4)$	$(PPh_3)_2$	1.809(17)	n

a M.I. Bruce, D.N. Duffy, M.G. Humphrey and A.G. Swincer, J. Organomet. Chem.
282, 383 (1985); b M.I. Bruce, D.N. Duffy, M.G. Humphrey and G.A. Koutsantonis,
unpublished results; c L.E. Smart, J. Chem. Soc., Dalton Trans. 390 (1976);
d M.I. Bruce, J.R. Rodgers, M.R. Snow and A.G. Swincer, J. Chem. Soc., Chem.
Commun. 271 (1981); e M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer,
Organometallics 4, 501 (1985); f J.M. Wisner, T.J. Bartczak and J.A. Ibers,
Inorg. Chim. Acta 100, 115 (1985); g M.I. Bruce and M.G. Humphrey, unpublished
results; h N.V. Raghavan and R.E. Davis, J. Cryst. Mol. Struct. 6, 73 (1976);
i M.I. Bruce, M.G. Humphrey, M.R. Snow and E. Tiekink, unpublished results;
j M.I. Bruce, F.S. Wong, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton.
Trans. 2203 (1982); k M.I. Bruce, M.G. Humphrey, E. Poczman, M.R. Snow and
E. Tiekink, unpublished results; l M.I. Bruce, C. Dean, M.G. Humphrey, G.A.
Koutsantonis and M.R. Snow, unpublished results; m M.I. Bruce, D.N. Duffy
and M.G. Humphrey, unpublished results; n M.I. Bruce, M.G. Humphrey, G.A.
Koutsantonis and B.K. Nicholson, unpublished results.
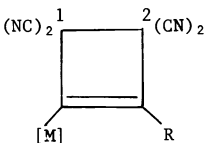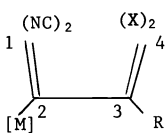
CYCLO-ADDITION REACTIONS OF METAL ACETYLIDES

A survey of the reactions of some platinum acetylide complexes includes several addition
and apparent insertion reactions (7). Our own studies on the synthesis and reactivity of
a series of ruthenium acetylide complexes led us to look at the reaction between tetra-
cyanoethylene (tcne) and $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$; unknown to us, Davison had commenced
a study of similar reactions of the analogous complex $Fe(C_2Ph)(CO)_2(\eta-C_5H_5)$ somewhat
earlier, and his first results were published (8) as we were waiting for structural char-
acterisation of our product. We soon found that these reactions are quite complex. They
proceed by initial formation of deeply coloured paramagnetic (ESR) intermediates, which
slowly transform into at least three types of isolable, diamagnetic complex. The nature of
the intermediates is not clear; in some cases, the ESR spectra can be interpreted in terms
of coupling of the unpaired electron to four N and one P nuclei. In others, rapid changes
in the ESR spectra indicate the formation and decay of more than one intermediate complex.

(1)   (2)
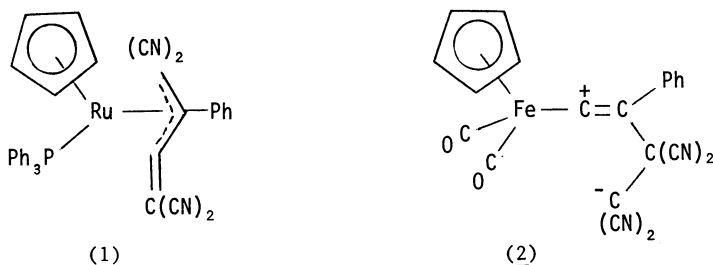
Although the product isolated from the first reaction that we studied was the 'allylic'
complex (1) (9), more detailed studies of these reactions, involving a range of olefins and
metal acetylides, have shown that cyclobutenyl, butadienyl and allyl complexes, of varying
stability, are formed sequentially (10). We have not yet obtained any evidence for the
formation of a zwitterionic complex of the type (2) proposed by Davison and Solar (8);
spectroscopic evidence suggests that (2) is indeed a cyclobutenyl complex, formed by formal
(2 + 2) cycloaddition of the olefin to the acetylide. While a concerted reaction of this
type is forbidden by the Woodward-Hoffmann rules, the observation of intermediates suggests

that this reaction proceeds stepwise. A notable feature of the C_4 ring in those complexes which have been studied crystallographically is the long C-C bond (see Table 2) opposite the ring C=C bond, which is the one that cleaves in the ring-opening reaction.

TABLE 2. Some Structural Parameters for σ-Cyclobutenyl and σ-Buta-1,3-dien-2-yl Complexes

Cyclobutenyl

M	R	M-C	C(1)-C(2)	Reference
$W(CO)_3(\eta-C_5H_5)$	Ph	2.202(9)	1.602(13)	a
$Ru(PPh_3)(L)(\eta-C_5H_5)$	Ph	2.07(2),	1.53(3),	b
$[L = (NC)C=C(CF_3)_2]$		2.01(2)	1.67(4)	
(complex 6)				

Butadienyl

M	R	X	M-C(2)	C(1)=C(2), C(3)=C(4)	C(2)-C(3)	Torsion angle*	Ref.
$Ru(dppe)(\eta-C_5H_5)$	Ph	CN	2.068(4)	1.382(5),1.362(4)	1.478(4)	80.6	c
$Ru(CNBu^t)(PPh_3)(\eta-C_5H_5)$	Ph	CN	2.074(3)	1.370(6),1.346(6)	1.484(6)	81.5	d
$Ru(CO)(PPh_3)(\eta-C_5H_5)$	Me	CF_3	2.106(5)	1.362(8),1.328(8)	1.493(8)	80.6	b
$Ru(PPh_3)_2(\eta-C_5H_5)$	Ph	†	2.063(8)	1.37(1) ,1.33(1)	1.52(1)	82.4	e
$Fe(CO)_2(\eta-C_5H_5)$	Ph	CN	1.972(2)	1.347(4),1.356(3)	1.476(3)	79.7	f

* C(1)C(2)/C(3)C(4)   † X_2 = H,$C_6H_4NO_2$-4

a M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, *J. Organomet. Chem.* 226, 1 (1982); b M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, unpublished results; c M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, *Organometallics* 4, 501 (1985); d M.I. Bruce, J.R. Rodgers, M.R. Snow and A.G. Swincer, *J. Chem. Soc., Chem. Commun.* 271 (1981); e M.I. Bruce, P.A. Humphrey, M.R. Snow and E. Tiekink, unpublished results; f M.I. Bruce, M.J. Liddell, M.R. Snow, A.G. Swincer and E. Tiekink, unpublished results

The reaction is limited at present to the more electrophilic olefins, as suggested by the results obtained with $4-XC_6H_4CH=C(CN)_2$; isolated yields of 88 and 14% of the cyclo-adduct were obtained with X = NO_2 and H, respectively, but no reaction occurred with X = NMe_2. Structural studies of some of these products suggest that steric effects control the direction of addition of the olefin to the acetylide group, the carbon bearing the bulkiest substituents being attached to the β-carbon of the acetylide ligand (11).

We have also used the olefins $CH(CO_2Me)=C(CN)(CO_2Me)$ and $(CF_3)_2C=C(CN)_2$ in these studies. Addition of the former gives products whose stereochemistry is consistent with the trans geometry of the olefin determined by ^{13}C NMR; chromatography of the cyclobutenyl complex (3) affords three isomeric forms which differ only in the degree of rotation of the ester groups. Heating of (3) gave the butadienyl complex (4), from which it is evident that the expected conrotatory ring-opening process has occurred; the presence of the transition metal substituent therefore does not affect this process (12).

(3)

(4)
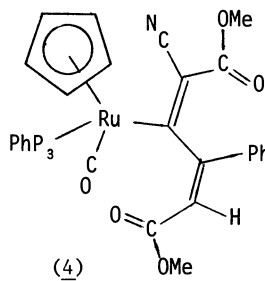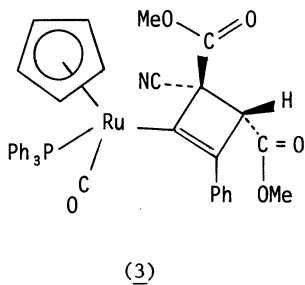
X-ray studies of several of the butadienyl complexes show that the C_4 system is significant-
ly non-planar (torsion angles about the central C–C bond are about 80°; see Table 2) and
that the C–C single and C=C double bonds are localised.   While the diene system does not
enter into cycloaddition reactions with substrates such as maleic anhydride, cyclohexene or
methyl vinyl ether, on heating or irradiation, chelation by attachment of the further C=C
to the metal centre affords a series of substituted exo-methyleneallyl complexes (5; Table
3).   The η^3-ligand has unusual structural and ^{13}C NMR parameters which suggest that a more
appropriate formulation for these complexes is as methylenemetallacyclobutenes, related to
Schrock's metallacyclobutadiene systems.

TABLE 3.   Some Structural and ^{13}C NMR Parameters for Allylic Complexes[a]
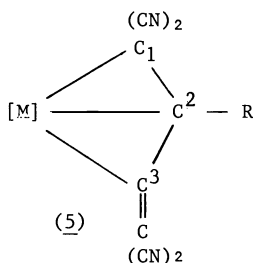
M	R	M–C (Å)			$\delta(^{13}C)$ (ppm)		
		C(1)	C(2)	C(3)	C(1)	C(2)	C(3)
$W(CO)_2(\eta-C_5H_5)$	Ph	2.285(8)	2.253(7)	2.075(8)	79.4	4.7	206.6
$Ru(PPh_3)(\eta-C_5H_5)$	Ph	2.231(4)	2.135(4)	1.919(5)	85.1	7.3	218.8
$Ru(PPh_3)(\eta-C_5H_5)$	Me	–			82.9	11.0	218.3

a M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, Organometallics 4, 501 (1985).

An unusual complex formed from $(CF_3)_2C=C(CN)_2$ and $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ is the deep
blue binuclear cyclobutenyl complex (6), in which a third molecule of the electrophilic
olefin bridges the two metal centres.   The intense colour may be a consequence of the
presence of the extended Ru–N=C–C=N–Ru system.   With the corresponding propynyl
complex, the reaction follows the more usual pattern to give the cyclobutenyl complex
(7) (13).
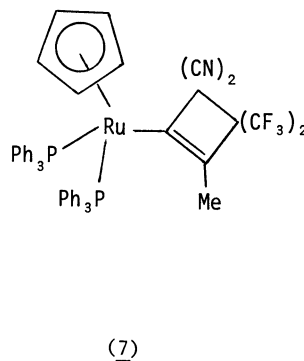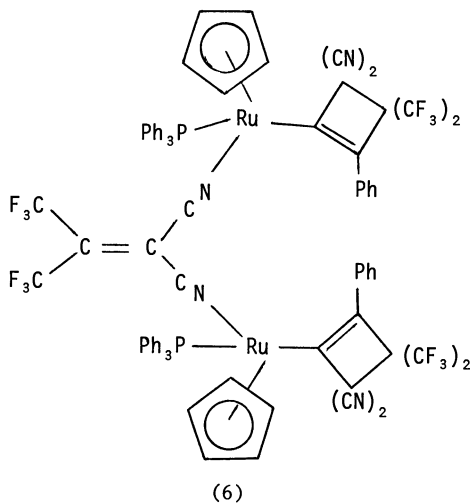
These reactions result from nucleophilic attack of the electron-rich metal acetylide (in
particular, the β-carbon) on the electrophilic olefins, and are not observed with convent-
ional alkynes such as C_2Ph_2.   The presence of the metal substituent serves to 'activate'
the C≡C triple bond, facilitating transfer of electron density to the β-carbon.   Work
continues to find metal-ligand combinations which will permit reaction between the acetylide
ligands and less electrophilic olefins.

NOVEL VINYLIDENE COMPLEXES

Transition metal acetylide complexes react with protons or alkylating agents to form the corresponding vinylidene complexes, which can be isolated in many cases (14). Some can be obtained directly from 1-alkynes and suitable metal-containing precursors. These compounds are of interest as containing the unstable tautomer of the alkyne, and undergo numerous reactions (Scheme 1). Although the α-carbon is highly electron-deficient and should be susceptible to nucleophilic attack, most of the kinetically stable vinylidene complexes fail to react with H^-, Me^-, MeO^- or MeS^-, for example, probably because of the steric protection afforded to the α-carbon by ligands surrounding the vinylidene ligand. However, deprotonation of the dppe complexes (8) results in intramolecular attack of the carbanion on the α-carbon, with formation of the tricyclic complexes (9) (15,16).

Scheme 1

$$[Fe'] = Fe(CO)(PPh_3)(\eta-C_5H_5)$$
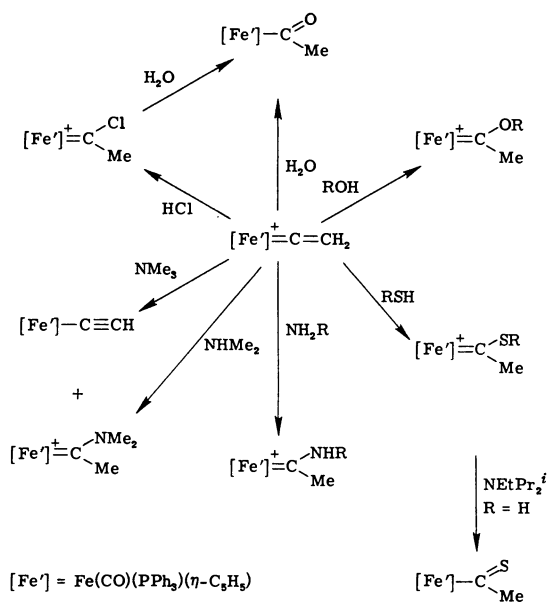
Some Reactions of a Cationic Vinylidene Complex[a]

M = Fe, Ru

(8)   (9)
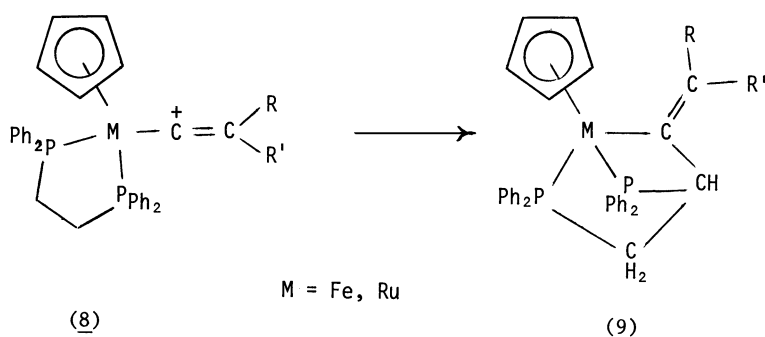
Extension of the protonation and alkylation reaction to other electrophiles has met with limited success. We have recently isolated cationic cycloheptatrienyl- (10) and aryldiazo-vinylidene complexes (11) from reactions between metal acetylides and tropylium or arenediazonium salts, respectively (17). Again, reactions of these derivatives with anionic or neutral nucleophiles has failed to elaborate the vinylidene ligand any further; indeed, the stability of the cations from which these are derived is manifest in several reactions, e.g. with Me^- or MeO^-, which result in regeneration of the parent metal acetylide.

---

a B.E. Boland-Lussier and R.P. Hughes, *Organometallics* **1**, 635 (1982). See also M.I. Bruce and A.G. Swincer, *Aust. J. Chem.* **33**, 1471 (1980), for related reactions of ruthenium complexes.

However, we have been able to alkylate, diprotonate and cyclometallate the aryldiazo-
vinylidene ligands to give (12), (13) and (14), respectively.

(10)   (11)   (12)

(13)   (14)   (15) X = Cl, Br, I
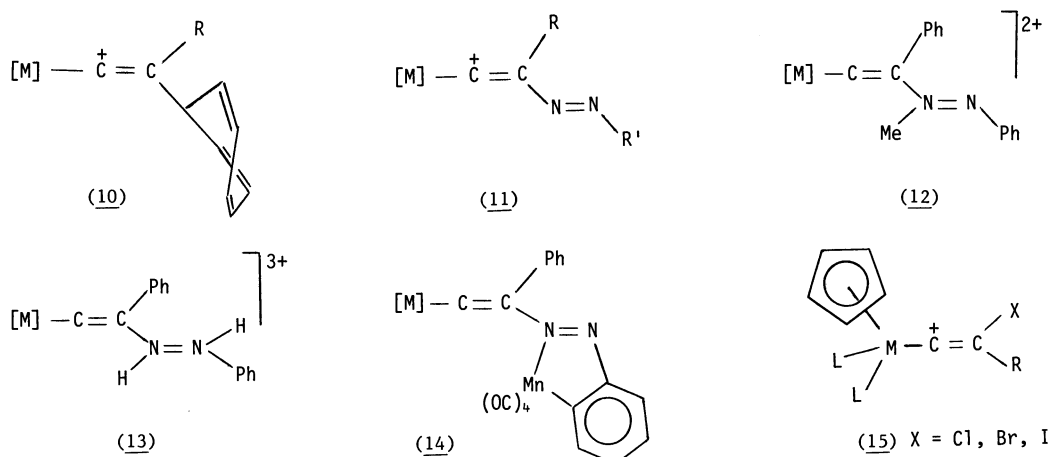
We were also somewhat surprised to find that addition of halogens (Cl$_2$, Br$_2$ or I$_2$) to the
iron, ruthenium or osmium acetylide complexes afforded almost quantitative yields of the deep
green halovinylidene complexes (15).   In some reactions of the phenylacetylides, the 4-
position of the phenyl group was also halogenated (18).   Again, these complexes are not
proving to be the sought-for doorway to functionalised vinylidene complexes: attempts to re-
place the halogen by metallation or substitution have so far given only the parent acetylide.

REACTIONS OF METAL ACETYLIDES WITH METAL COMPLEXES, AND RELATED CHEMISTRY

A fruitful source of novel and unusual structures in the early years of organometallic chem-
istry was the addition of metal substrates to acetylenes;   new examples continue to be
found, although rationalisation of their formation is often more with hindsight.   The first
studies of similar reactions with metal acetylides were carried out many years ago, although
as with simple alkynes, reactions with iron or cobalt carbonyls, for example, give numerous
products in small to infinitesimal yields.   Early studies of the reaction of Fe$_2$(CO)$_9$ with
Fe(C$_2$Ph)(CO)$_2$(η-C$_5$H$_5$) resulted in the identification of the trinuclear cluster (16) (19, 20),
while the similar reactions of Group 6 and ruthenium analogues have since been described
(21, 22).   Evidence for the C≡C triple bond retaining its usual complexing powers towards
cobalt carbonyl is found in the formation of (17a) and (17b) in the reactions of the parent
acetylides with Co$_2$(CO)$_8$ (23, 24);   thermal conversion of the latter to (18) has subsequent-
ly been achieved (24).

(16)

(17)   a, M = Mn(CO)$_4$(PCy$_3$)   (ref. 23)
       b, M = Fe(CO)$_2$(η-C$_5$H$_5$) (ref. 24)

(18)   (19)
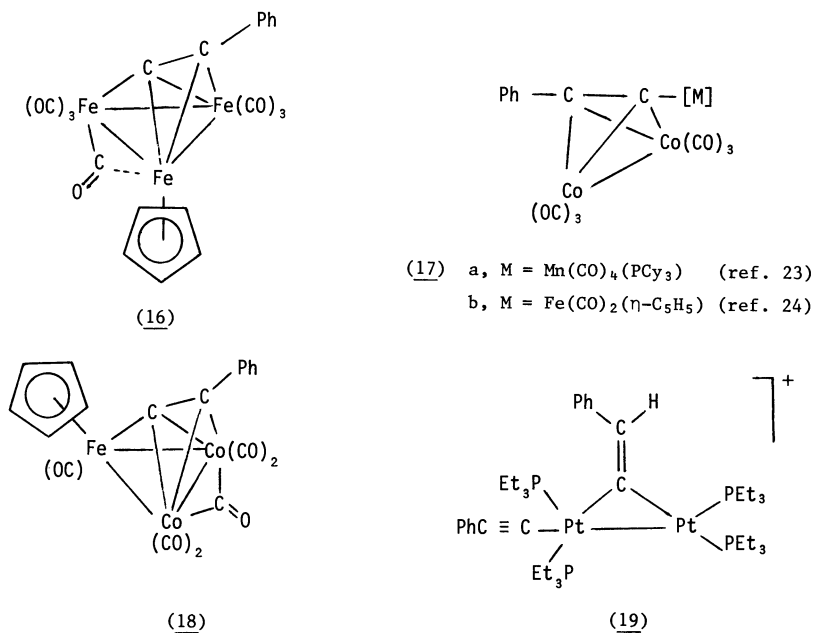
We have studied the addition of hydrogen to cluster-bound acetylides as a possible route to vinylidene complexes. The addition of $[PtH(PEt_3)_2(OCMe_2)]^+$ to *trans*-$Pt(C_2Ph)_2(PEt_3)_2$ gave the binuclear complex (19) (25), and the facile conversion of $Co_2Ru(\mu_3-HC\equiv CCMe_3)(\mu-CO)(CO)_8$ (20) to $Co_2Ru(\mu_3-C=CHCMe_3)(CO)_9$ (21) was demonstrated by Bernhardt and Vahrenkamp (26); Silvestre and Hoffmann (27) have recently made a theoretical study of the transformation of 1-alkynes to vinylidenes on metal centres.
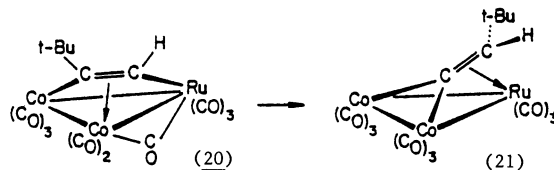
Addition of hydride to μ_3-acetylide complexes (22) would be expected to open the trigonal-bipyramidal C_2M_3 cluster to the open square-pyramidal arrangement (23), with concomitant addition of the hydrogen to the α-carbon. The resulting anion can be protonated to effect the addition of H_2 ($H^- + H^+$) to the original cluster. It has been known for some years that addition of H_2 to $Ru_3(\mu-H)(\mu_3-C_2CMe_3)(CO)_9$ gives $Ru_3(\mu-H)_3(\mu_3-CCH_2CMe_3)(CO)_9$ by addition of two H to the β-carbon; the intermediate vinylidene complex was not detected (28). However, sequential addition of hydride and $[O\{Au(PPh_3)\}_3]^+$ to the cluster acetylide gave complex (24) corresponding to addition of H_2 and '$Au_2(PPh_3)_2$' (isolobal with H_2) to the cluster (29).
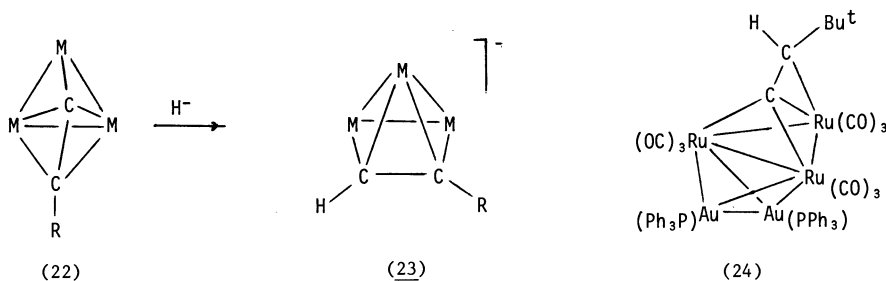
Another surprising example was found during our studies of the reactivity of the open Ru_5 cluster (25; Scheme 2) (30). The extended interaction of the diphenylphosphino-acetylide ligand with the five metal atoms was expected to result in considerable activation towards other small molecules. In cyclohexane solution, (25) reacts with dihydrogen (1 atm., r.t.)

Scheme 2
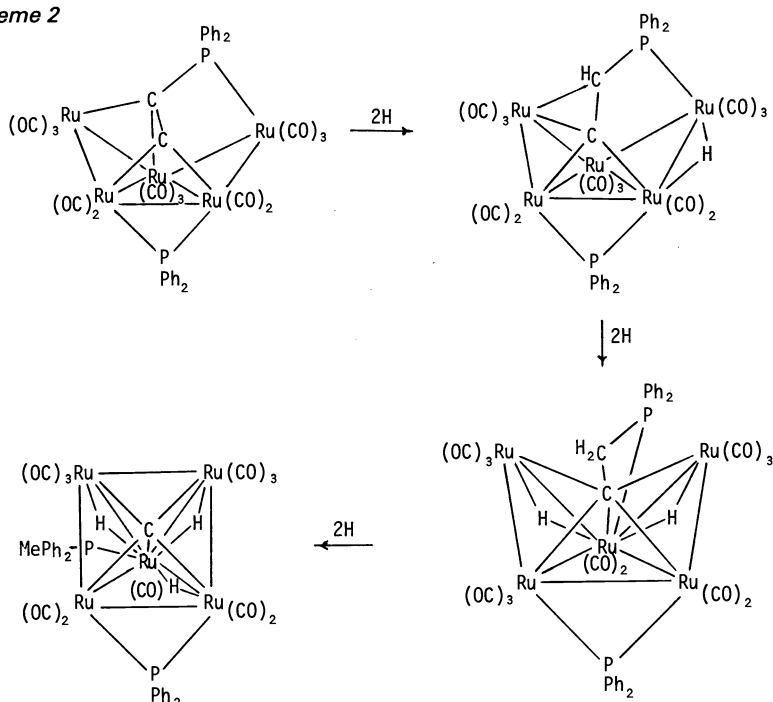
Reduction of an acetylide to C + Me on an Open Ru_5 Cluster (ref. 31)

to take up successively one, two and three molecules of H_2, forming complexes (26), (27) and (28), respectively; the first and last of these have been fully characterised crystallo-graphically (31).   In the context of this paper, the most interesting features of this reaction are the successive addition of one, two and three hydrogen atoms to the β-carbon of the cluster-bound acetylide to give C=CHPPh$_2$, C-CH$_2$PPh$_2$ and finally (C + CH$_3$PPh$_2$) ligands attached to the cluster.   Scheme 2 also shows the cleavage of the acetylenic C≡C bond in the last step with concomitant formation of a carbido cluster derived from Ru$_5$C(CO)$_{15}$; the unusual course of this reduction of a C≡C triple bond to carbon and methyl is determined by the formation of strong metal-metal bonds.

REFERENCES

1. A.N. Nesmeyanov, L.G. Makarova and I.V. Polovyanyuk, J. Organomet. Chem. 22, 707 (1970).
2. H. Lehmkuhl, J. Grundke, G. Schroth and R. Benn, Z. Naturforsch. 39b, 1050 (1984).
3. T.-W. Lai and A. Sen, Organometallics 3, 866 (1984).
4. T. Blackmore, M.I. Bruce and F.G.A. Stone, J. Chem. Soc., Dalton Trans. 106 (1974).
5. Y. Tohda, K. Sonogashira and N. Hagihara, J. Chem. Soc., Chem. Commun. 54 (1975).
6. N. Kostic and R. Fenske, Organometallics 1, 974 (1982).
7. M.H. Chisholm and L.A. Rankel, Inorg. Chem. 16, 2177 (1977).
8. A. Davison and J.P. Solar, J. Organomet. Chem. 166, C13 (1979).
9. M.I. Bruce, J.R. Rodgers, M.R. Snow and A.G. Swincer, J. Chem. Soc., Chem. Commun. 271 (1981).
10. M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, Organometallics 4, 494, 501 (1984).
11. M.I. Bruce, P.A. Humphrey, M.R. Snow and E. Tiekink, unpublished results.
12. M.I. Bruce and D.N. Duffy, unpublished results.
13. M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, unpublished results.
14. M.I. Bruce and A.G. Swincer, Adv. Organomet. Chem. 22, 59 (1983).
15. R.D. Adams, A. Davison and J.P. Selegue, J. Am. Chem. Soc. 101, 7232 (1979).
16. M.I. Bruce, M.G. Humphrey and E. Poczman, unpublished results.
17. M.I. Bruce, D.N. Duffy, M.G. Humphrey and G.A. Koutsantonis, unpublished results.
18. M.I. Bruce, G.A. Koutsantonis and B.K. Nicholson, unpublished results.
19. K. Yasufuku, K. Aoki and H. Yamazaki, Bull. Chem. Soc. Jpn 48, 1616 (1975).
20. R.J.F. May, B.Sc. Hons. Thesis, Univ. Bristol (1971).
21. N.A. Ustynyuk, V.N. Vinogradova, V.N. Korneva, Yu.L. Slovokhotov and Yu.T. Struchkov, Koord. Khim. 9, 631 (1983).
22. O.M. Abu Salah, M.I. Bruce, R.E. Davis and N.V. Raghavan, J. Organomet. Chem. 64, C48 (1974).
23. G.A. Carriedo, V. Riera, D. Miguel, A.M. Manotti Lanfredi and A. Tiripicchio, J. Organomet. Chem. 272, C17 (1984).
24. M.I. Bruce, D.N. Duffy and M.G. Humphrey, unpublished results.
25. D. Afzal, P.G. Lenhert and C.M. Lukehart, J. Am. Chem. Soc. 106, 3050 (1984).
26. W. Bernhardt and H. Vahrenkamp, Angew. Chem. 96, 139 (1984); Angew. Chem., Int. Ed. Engl. 23, 141 (1984).
27. J. Silvestre and R. Hoffmann, J. Am. Chem. Soc. 107, 0000 (1985).
28. M. Castiglioni, G. Gervasio and E. Sappa, Inorg. Chim. Acta 49, 217 (1981).
29. M.I. Bruce, E. Horn, O. bin Shawkataly and M.R. Snow, J. Organomet. Chem. 280, 289 (1985).
30. M.I. Bruce, B.W. Skelton, A.H. White and M.L. Williams, J. Chem. Soc., Dalton Trans. 1229 (1985).
31. M.I. Bruce, B.W. Skelton, A.H. White and M.L. Williams, J. Chem. Soc., Chem. Commun. 744 (1985).