

Carbenes, carbides, and carbon. Ten years of transition metal–acetylene chemistry

[The G.J. Burrows Memorial Lecture]

Michael I. Bruce

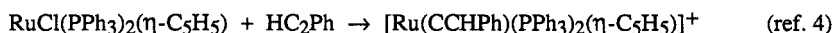
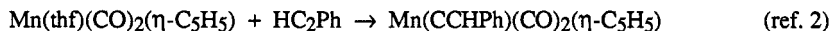
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5000

Abstract

The lecture describes some of our studies into the reactivity of several transition metal complexes towards a wide variety of alkynes and related compounds. The results include (i) reactions of metal acetylides with electrophiles to give vinylidenes or cycloadducts; (ii) oligomerisation of alkynes at mononuclear ruthenium centres to give novel tri- and tetra-mers; (iii) oxidative tetra- and pentamerisation of phenylacetylide to unusual metalla-polycyclic systems; (iv) transformations of cluster-bound acetylides to alkynes and vinylidenes; (v) reactivity of a phosphino-acetylide on an open Ru₃ cluster.

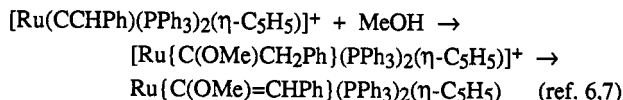
ISOMERISATION OF 1-ALKYNES TO VINYLIDENES AND THEIR REACTIONS

The formation of transition metal complexes containing unsaturated carbenes (vinylidenes) (ref. 1) by reaction of 1-alkynes with appropriate precursors was described many years ago by several groups:

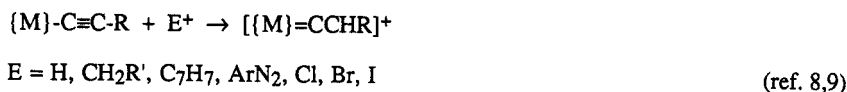


The ready deprotonation of cationic vinylidene complexes to the corresponding acetylides, and conversely the strongly nucleophilic properties of the latter, were early recognised, and later rationalised by an extended Huckel MO study (ref. 5).

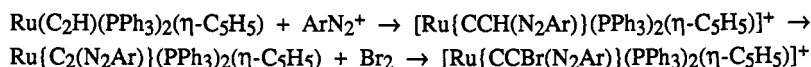
Attack by nucleophiles on the vinylidene C_α provided a route to carbene complexes and related vinyl derivatives by deprotonation:



Addition of electrophiles to C_β of the acetylide ligand gave a range of novel substituted vinylidenes, and represents new C–X bond making reactions for X = H, C, N, halogen:



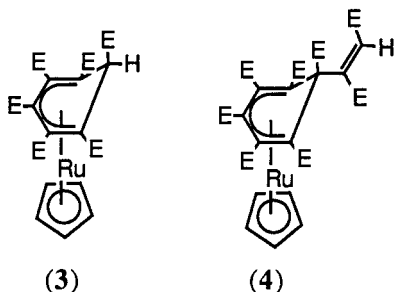
In principle, sequential application of the electrophilic addition and deprotonation reactions to ethynyl complexes could enable unusual acetylide and vinylidene derivatives to be obtained:



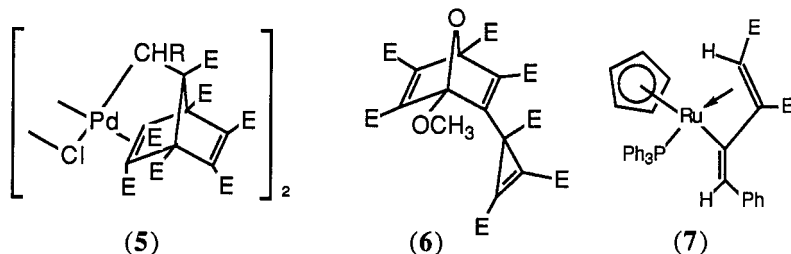
OLIGOMERISATION OF ALKYNES AT MONONUCLEAR RUTHENIUM CENTRES

The insertion of alkynes into Ru-H and Ru-C bonds was first studied many years ago and proved to be a rich source of unusual complexes containing vinyl, butadienyl, and pentatrienyl ligands, in addition to other more highly rearranged systems (ref. 10). The ready loss of one PPh₃ ligand from the precursor Ru(PPh₃)₂(η-C₅H₅) complexes to generate a vacant coordination site facilitated the incorporation of more than one alkyne into the products, as it facilitates the coordination of ester, acyl, or unsaturated groups to the metal.

Further reactions of these complexes, e.g., $\text{Ru}\{\overline{\text{CE=CHC(O)OMe}}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ or $\text{Ru}\{\overline{\text{CE=CECE=CH}}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (E = CO₂Me) (ref. 11) with C₂(CO₂Me)₂ resulted in incorporation of one or two more alkyne molecules to give highly substituted η⁵-cyclohexadienyl complexes (3) and (4):



The reactions recall the tri- and tetra-merisation of C₂(CO₂Me)₂ on palladium systems described by Maitlis and coworkers (ref. 12) in the 1970's, which were found to give derivatives of substituted norbornadienes such as (5). Also, the alkyne itself tetramerises on heating to give the cyclopropenylnorbornadiene (6):

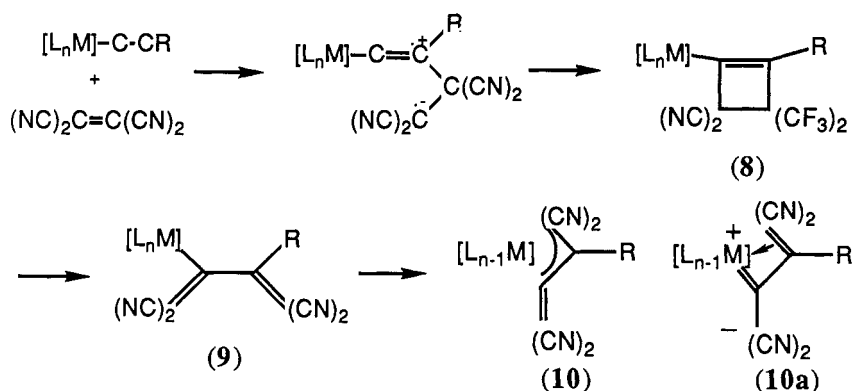


In our case, the cyclisation presumably proceeds by displacement of the remaining PPh₃ ligand and cyclisation of the η⁵-dienyl system formed by coupling of the butadienyl and alkyne moieties on the metal. Similarly, addition of the fourth alkyne to the dienyl intermediate results in formation of a chain too long to allow the coordination of the terminal C=C double bond; cyclisation then forms the vinylcyclohexadienyl ligand found in (4).

Reactions with 1-alkynes proceed somewhat differently (ref. 14). The structure of the product (7) obtained from $\text{Ru}\{\overline{\text{C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})(\text{OMe})}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ and HC₂Ph shows that, in contrast to the disubstituted alkynes, initial isomerisation to the vinylidene is followed by coupling to give an allylic system. A possible explanation is that dissociation of the ester carbonyl group rather than the PPh₃ ligand occurs, generating a site too small to accommodate an η²-alkyne, but large enough for the linear vinylidene tautomer.

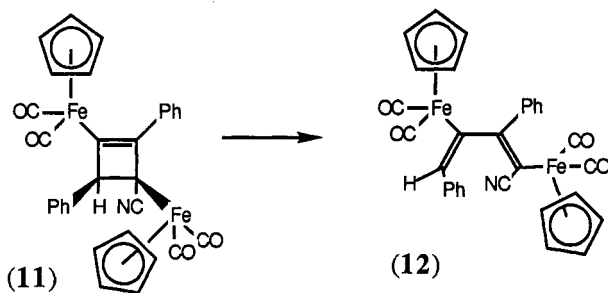
CYCLOADDITION REACTIONS OF METAL ACETYLIDES WITH OLEFINS

The (2 + 2) cycloaddition of olefins to metal acetylides proceeds via deeply coloured paramagnetic intermediates in many cases, which more or less rapidly (seconds to hours) transform to diamagnetic cyclobutenyl complexes (8). In turn, these undergo the anticipated ring-opening reactions to form butadienyl derivatives (9). Where a ligand can be lost from the metal coordination sphere, either by heating or irradiation, these complexes may be converted to allylic complexes (10) (ref. 15):



The allylic complexes are characterised by short M-C distances to a strongly deshielded carbon atom (δ ca 200), data which are probably best interpreted in terms of the dipolar structure (10a). These complexes are particularly common with the second and third row transition metals, and join the growing class of $\eta^n(n+1e)$ -unsaturated ligands, which now include $\eta^2(3e)$ -vinyl, $\eta^3(4e)$ -allyl and $\eta^4(5e)$ -butadienyl ligands; the $\eta^2(4e)$ -butatrienyl ligand is also related.

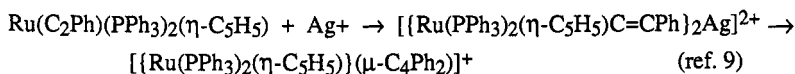
The C_4 chain in (9) cannot become planar, probably because of steric interactions between the substituents; consequently the C-C and C=C bonds are localised. Of some interest is the thermal cyclobutenyl \rightarrow butadienyl ring-opening reaction, which, if concerted, should be conrotatory if the Woodward-Hoffmann rules are obeyed, or more accurately, if the σ -bonded transition metal group does not perturb the system. Structural studies of appropriately-substituted derivatives allowed a determination of the stereochemistry of this reaction. In fact, an earlier report (ref. 16) which describes the conversion of the dimetallic complex (11) to its butadienyl isomer (12) with accompanying structural identifications of the two complexes did not comment on this aspect of the reaction; the ring-opening was conrotatory in this case:

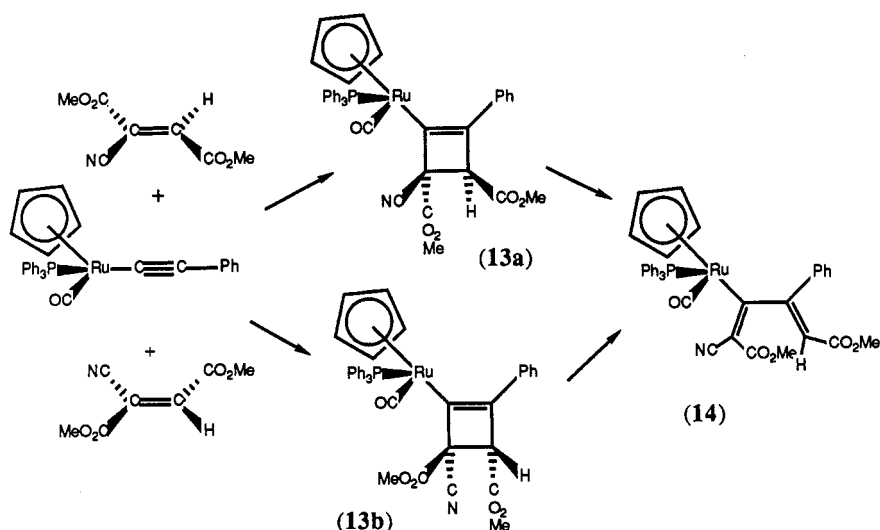


We have studied complexes formed from the olefin *trans*- $CH(CO_2Me)=C(CN)(CO_2Me)$, which formed the two readily separable diastereomers (13a and b) (chiral at Ru), consistent with the two possible approaches of the olefin to the C \equiv C triple bond (ref. 17). Both isomers form the same butadienyl complex (14) on heating. Again, the structural results are consistent with a conrotatory ring-opening process, which is followed by further rotation about the M-C and C-C bonds to accommodate the bulky substituents. The conclusion is that the transition metal substituent does not affect the mode of ring-opening, in spite of the interaction of the metal d orbitals with the vinyl systems indicated by theory.

OXIDATIVE COUPLING OF VINYLIDENE OR ARYLACETYLIDE RESIDUES

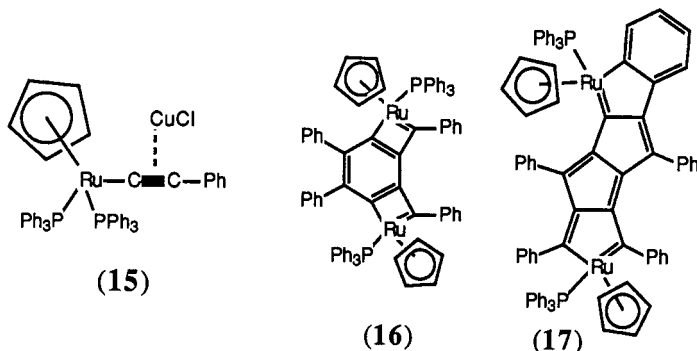
Oxidative coupling of the vinylidene ligands, first demonstrated in the synthesis of the iron complex $[\{Fe(dppe)(\eta-C_5H_5)\}_2(\mu-C_4Me_2)]^+$ by oxidation of the mononuclear methylvinylidene complex with PhIO (ref. 18), has been shown to proceed via a cationic silver(I) complex of the acetylide when Ag^+ is used as the oxidising agent (ref. 9). In this case, prior formation of the mononuclear vinylidene is not required:





Related complexes have been described for Cu, Ag, and Au before (refs. 19,20), and our recent studies have shown that similar derivatives containing Pd(II) or Hg(II) can be made (ref. 17). Coordination of copper(I) to metal acetylides occurs by η^2 -bonding of the $\text{C}\equiv\text{C}$ triple bond to the Group 11 atom; crystallographic characterisation of several complexes of this type, such as $\text{Ru}\{\eta^2\text{-C}_2\text{Ph}(\text{CuCl})\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (15), has been reported (ref. 20).

Attempted preparation of the silver(I) analogue of (15) by the reaction between $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ and AgC_2Ph gave a complex mixture of products which included Ag, $\{\text{AgCl}(\text{PPh}_3)\}_4$, and two binuclear complexes which have been crystallographically characterised as (16) and (17) (ref. 11):

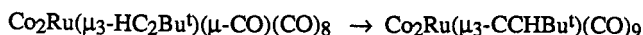


Bond localisation in the polycyclic systems is induced by the presence of Ru-C and Ru=C bonds. As can be seen, the two complexes contain dimetalla-polycyclic systems which are unprecedented; the benzene nucleus in (16) is fused to two ruthenacyclobutadiene rings, while (17) contains a methylenepentylene system fused to ruthenacyclopentadienes. The latter is the first example of a stable pentalene-metal complex which does not contain the ring system η -bonded to the metal.

The route by which these intriguing complexes are formed is still a matter of speculation. However, the observations described above on the formation and subsequent dimerisation of silver-acetylide complexes can be extended, on paper at least, by incorporation of further reactions with AgC_2Ph to form (16).

TRANSFORMATIONS OF CLUSTER-BOUND ACETYLIDE LIGANDS

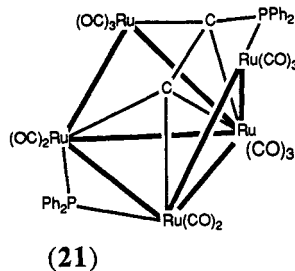
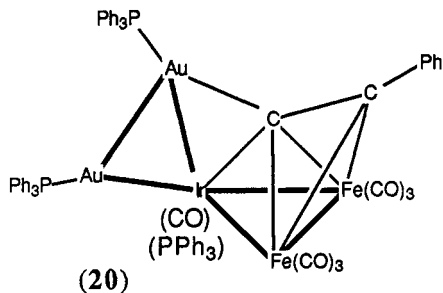
Isomerisation of terminal alkynes to vinylidenes on certain cluster complexes has been demonstrated by Vahrenkamp's elegant studies of a cobalt-ruthenium system:



(ref. 21)

An early venture of ours into this field involved auration of $[\text{Ru}_3(\mu_3\text{-C}_2\text{Bu}^t)(\text{CO})_9]^-$ with $[\{\text{Au}(\text{PPh}_3)\}_3\text{O}]^+$, which afforded the complexes $\text{Ru}_3(\mu\text{-AuPPh}_3)(\mu_3\text{-C}_2\text{Bu}^t)(\text{CO})_9$ and $\text{Ru}_3\{\mu\text{-Au}_2(\text{PPh}_3)_2\}(\mu_3\text{-CCHBu}^t)(\text{CO})_9$ (ref. 22); in the latter, the hydrocarbon ligand is CCHBu^t , whereas addition of H_2 to the parent hydrido-acetylide cluster gave $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-CCH}_2\text{Bu}^t)(\text{CO})_9$ (ref. 23). In this case, the usual isolobal equivalence between H and $\text{Au}(\text{PR}_3)$ is not followed.

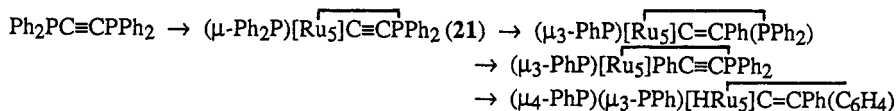
The new cluster $\text{Fe}_2\text{Ir}(\mu_3\text{-C}_2\text{Ph})(\text{CO})_8(\text{PPh}_3)$ adds H^- to give the μ_3 -alkyne complex $[\text{Fe}_2\text{Ir}(\mu_3\text{-HC}_2\text{Ph})(\text{CO})_8(\text{PPh}_3)]^-$ (in an interesting reversal of the normal reactivity of phenylacetylide!), and then H^+ to give the hydrido-alkyne derivative $\text{Fe}_2\text{Ir}(\mu\text{-H})(\mu_3\text{-HC}_2\text{Ph})(\text{CO})_8(\text{PPh}_3)$ (18), which readily isomerised on heating to the vinylidene $\text{Fe}_2\text{Ir}(\mu\text{-H})(\mu_3\text{-CCHPh})(\text{CO})_8(\text{PPh}_3)$ (19) (ref. 11). Addition of H_2 gave (19) directly, while addition of H^+ followed by $[\text{Au}(\text{PPh}_3)]^+$, gave $\text{Fe}_2\text{Ir}(\mu\text{-AuPPh}_3)(\mu_3\text{-HC}_2\text{Ph})(\text{CO})_8(\text{PPh}_3)$, the isolobal equivalent of (18). Extension of the reaction to $\text{Au}_2(\text{PPh}_3)_2$ gave the unusual complex (20), in which the coordination of one $\text{Au}(\text{PPh}_3)$ group to C_α of the acetylide fragment possibly models an intermediate stage of the addition of H_2 to the same cluster.



REACTIONS OF AN OPEN Ru_5 CLUSTER CONTAINING A PHOSPHINO-ACETYLIDE LIGAND

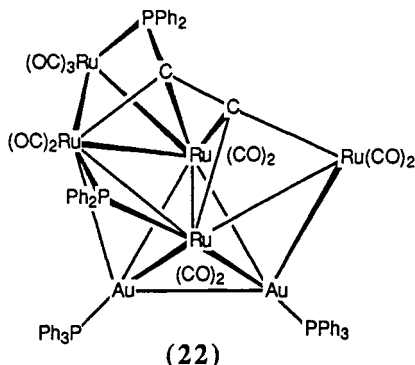
We have previously described the cluster transformations occurring in reactions between $\text{Ru}_5(\mu_5\text{-}\eta^2\text{-P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$ (21) [obtained by pyrolysis of $\{\text{Ru}_3(\text{CO})_{11}\}_2(\mu\text{-dppa})$; $\text{dppa} \equiv \text{C}_2(\text{PPh}_2)_2$] with CO, and the unusual stepwise "reduction" of C-C to $(\text{C} + \text{CH}_2)$ when it is treated with H_2 under mild conditions (ref. 24). Under pressure, the alkyne-hydrido cluster $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-HC}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{10}$ was formed. Pyrolysis under CO gave the C_2 complex $\text{Ru}_4(\mu_4\text{-C}_2)(\mu\text{-PPh}_2)_2(\text{CO})_{12}$.

As expected, the bridging ligand in (21) is very reactive (ref. 25). Further pyrolysis of (21) has given several complexes in which the net transformations

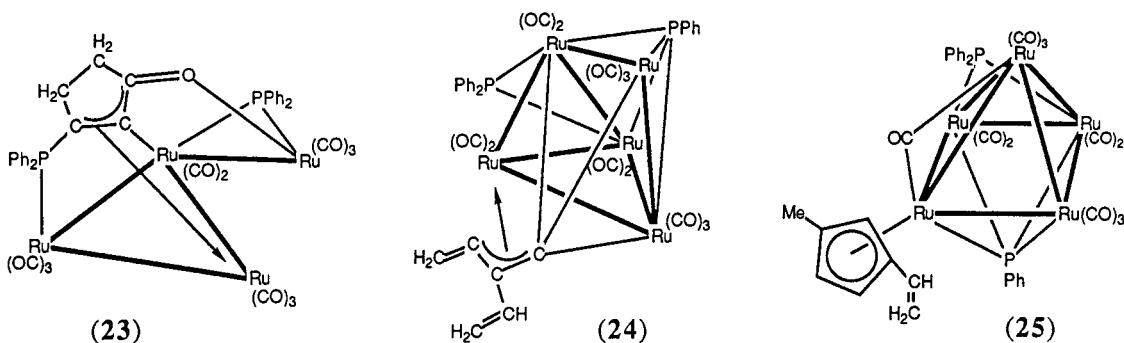


have occurred.

Opening of the cluster to the "scorpion" conformation occurred when (21) was treated with HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$); addition of the 4e ($\text{H} + \text{Cl}$ or Br) or 6e ($\text{H} + \text{I}$) gave clusters containing $\mu\text{-X}$ or $\mu_3\text{-X}$ ligands respectively. A similar product was obtained from the reaction with $\text{AuCl}(\text{PPh}_3)$, in which the $\text{Au}(\text{PPh}_3)$ fragment probably bridges the same Ru-Ru bond as does H in the halide complexes. Addition of $\text{Au}_2(\text{PPh}_3)_2$, however, gave (22) which cannot be related structurally to any of the products obtained from (21) and H_2 at this stage.



Reactions between (21) and ethene have given the Ru_4 and Ru_5 complexes (23-25), in which the organic ligands are formed by combination of the C_2 fragment with one, two, or three molecules of C_2H_4 , respectively. In (23), a molecule of CO has also been incorporated, whilst the substituted cyclopentadienyl ligand in (25) could conceivably have been formed by cycloaddition of the third C_2H_4 molecule to the C_6 ligand in (24). In these two complexes, the C-P bond has been cleaved, but it has not been possible to determine when this occurred.



Acknowledgements

I am pleased to have the opportunity to thank my coworkers named in the references for their enthusiasm and hard work, and the crystallographic groups led by Drs M.R. Snow and E.R.T. Tiekink (Adelaide), B.K. Nicholson (Waikato) and Professor A.H. White (Western Australia) for their essential contributions. Continued support from the Australian research Grants Scheme (now the Australian research Council) is also gratefully acknowledged.

REFERENCES

1. M.I. Bruce and A.G. Swincer, *Adv. Organomet. Chem.*, **22**, 59 (1983).
2. A.B. Antonova, N.E. Kolobova, P.V. Petrovsky, B.V. Lokshin and N.S. Obezyuk, *J. Organomet. Chem.*, **137**, 55 (1977).
3. A. Davison and J.P. Solar, *J. Organomet. Chem.*, **155**, C8 (1978).
4. M.I. Bruce and R.C. Wallis, *J. Organomet. Chem.*, **161**, C1 (1978).
5. N.M. Kostic and R.F. Fenske, *Organometallics*, **1**, 974 (1982).
6. M.I. Bruce and A.G. Swincer, *Aust. J. Chem.*, **33**, 1471 (1980).
7. M.I. Bruce, D.N. Duffy, M.G. Humphrey, and A.G. Swincer, *J. Organomet. Chem.*, **282**, 383 (1985).
8. M.I. Bruce, G.A. Koutsantonis, M.J. Liddell, and B.K. Nicholson, *J. Organomet. Chem.*, **217** (1987); M.I. Bruce, M.G. Humphrey, and M.J. Liddell, *J. Organomet. Chem.*, **321**, 91 (1987); M.I. Bruce, G.A. Koutsantonis, and M.J. Liddell, *J. Organomet. Chem.*, **326**, 247 (1987).
9. S. Abbott, S.G. Davies, and P. Warner, *J. Organomet. Chem.*, **246**, C65 (1983).
10. T. Blackmore, M.I. Bruce, and F.G.A. Stone, *J. Chem. Soc. Dalton Trans.*, 106 (1974); M.I. Bruce, R.C.F. Gardner, J.A.K. Howard, F.G.A. Stone, M. Welling, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 612 (1977).
11. M.I. Bruce, G.A. Koutsantonis, B.K. Nicholson, and E.R.T. Tiekink, unpublished work.
12. A. Konietzky, P.M. Bailey, and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 78 (1975).
13. J.C. Kauer and H.E. Simmons, *J. Org. Chem.*, **33**, 2720 (1968).
14. M.I. Bruce and M.P. Cifuentes, unpublished work.
15. M.I. Bruce, T.W. Hambley, M.R. Snow, and A.G. Swincer, *Organometallics*, **4**, 494 (1985).
16. N.E. Kolobova, T.V. Rozantseva, Yu. T. Struchkov, A.S. Batsanov, and V.I. Bakhmutov, *J. Organomet. Chem.*, **292**, 247 (1985).
17. M.I. Bruce, M.J. Liddell, and E.R.T. Tiekink, unpublished work.
18. R.S. Iyer and J.P. Selegue, *J. Am. Chem. Soc.*, **109**, 910 (1987).
19. M.I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organomet. Chem.*, **42**, C107 (1972). Abu Salah, M.I. Bruce, R.E. Davis, and N.V. Raghavan, *J. Organomet. Chem.*, **64**, C48 (1974).
20. G.A. Carriedo, D. Miguel, V. Riera, X. Solans, M. Font-Alba, and M. Coll, *J. Organomet. Chem.*, **299**, C43 (1986); G.A. Carriedo, D. Miguel, V. Riera, and X. Solans, *J. Chem. Soc., Dalton Trans.*, 2867 (1987).
21. E. Roland, W. Bernhardt, and H. Vahrenkamp, *Chem. Ber.*, **118**, 2858 (1985).
22. M.I. Bruce, E. Horn, O. bin Shawkataly, and M.R. Snow, *J. Organomet. Chem.*, **280**, 289 (1985).
23. S. Aime, G. Gervasio, L. Milone, E. Sappa, and M. Franchini-Angela, *Inorg. Chim. Acta*, **26**, 223 (1978).
24. M.I. Bruce, M.L. Williams, B.W. Skelton, and A.H. White, *J. Organomet. Chem.*, in press.
25. M.I. Bruce, B.K. Nicholson, M.J. Liddell, E.R.T. Tiekink, B.W. Skelton, and A.H. White, unpublished work.