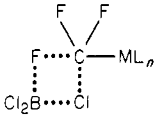
$$[Cl_3BF]^-[F_2C{=}ML_n]^+$$

3



4

chlorocyclopropene with BBr_3 to afford tetrabromocyclopropene.[15,16]

Mono- and dihalomethyl complexes can also be prepared by this method from the appropriate fluoromethyl complexes[17] (eq 3). These complexes were characterized by

$$Mn(CO)_5CH_nF_{3-n} + BX_3 \xrightarrow[n = 1, 2]{} Mn(CO)_5CH_nX_{3-n} + BF_nX_{3-n} \quad (3)$$

their NMR, IR, and mass spectra and the thermally stable chloro derivatives by elemental analysis. The spectroscopic properties[18] of $Mn(CO)_5CH_2Cl$ agree with those recently reported[6b] for this complex. The previously unreported complex $Mn(CO)_5CH_2Br$ exhibits a singlet in its ^1H NMR spectrum at δ 3.29. The ^1H NMR spectra of the dihalo complexes $Mn(CO)_5CHX_2$ (X = Cl,[19] Br) show singlets at δ 6.62 and 6.32, respectively. Again the carbonyl infrared bands are nearly coincident with those of the fluoromethyl starting materials.

Extension of this reaction to other transition-metal systems has been briefly explored. Reaction of $CpFe(CO)_2CF_3$[4b] with 1 equiv of BCl_3 affords $CpFe(CO)_2CCl_3$. This compound was crystallized from pentane at −78 °C and characterized by its IR, ^1H NMR, and mass spectra[20] and by the evolution of BF_3 gas from the reaction mixture. Exposure of a CH_2Cl_2 solution of $CpFe(CO)_2CCl_3$ to excess NH_3 results in a rapid reaction according to eq 4 to yield

$$CpFe(CO)_2CCl_3 + 4NH_3 \rightarrow CpFe(CO)_2CN + 3NH_4Cl \quad (4)$$

the known $CpFe(CO)_2CN$ complex,[21] which was characterized by its IR, NMR, and mass spectra. Ammonium chloride was identified by its mull IR spectrum.[22] Similarly, hydrolysis of $CpFe(CO)_2CCl_3$ in MeCN solution affords $[CpFe(CO)_3]^+$.[23] These types of solvolysis reactions have previously been observed[5,24] only for dihalocarbene transition-metal complexes. Electrophilic halogen exchange provides a mild, high yield synthetic route to a variety of α-haloalkyl complexes. These complexes are much more reactive than their thermally robust fluorocarbon homologues.

Acknowledgment. T.G.R. is the recipient of an NSF Predoctoral Fellowship. This research was sponsored by the NSF through Grant CHE-8204401.

Registry No. 1, 20774-63-4; 2, 86392-62-3; $Mn(CO)_5CF_3$, 13601-14-4; $Mn(CO)_5CHF_2$, 15022-34-1; $Mn(CO)_5CH_2F$, 15337-23-2; $CpFe(CO)_2CF_3$, 52409-72-0; $Mn(CO)_5CCl_3$, 86392-59-8; $Mn(CO)_5CBr_3$, 86392-60-1; $Mn(CO)_5CI_3$, 86392-61-2; $Mn(CO)_5CH_2Br$, 86392-63-4; $Mn(CO)_5CHCl_2$, 86392-64-5; $Mn(CO)_5CHBr_2$, 86392-65-6; $CpFe(CO)_2CCl_3$, 86392-66-7; $CpFe(CO)_2CN$, 12152-37-3; $CpFe(CO)_3^+$, 32660-74-5; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BI_3, 13517-10-7; NH_3, 7664-41-7.

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[19] Anal. Calcd for $C_6HCl_2MnO_5$: C, 25.84; H, 0.36; Cl, 25.42. Found: C, 25.90; H, 0.33; Cl, 25.69. IR (C_6H_{14}): 2127 (w), 2036 (s), 2009 (m) cm^{-1}.

[20] IR (C_5H_{12}): 2049 (s), 2006 (vs) cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 5.27. Mass spectrum (15 eV), *m/e* 294.

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Alkylidyne–Alkyne Coupling on Triruthenium Clusters. A Potential Model for Fischer–Tropsch Chain Growth

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Summary: The clusters $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe, Me, Ph) react with alkynes C_2R_2 to form the corresponding alkene $C_2H_2R_2$ and $HRu_3(\mu_3\text{-}\eta^3\text{-}CXCRCR)(CO)_9$. Terminal alkynes yield mixtures of the two possible isomers in ratios dependent upon the steric bulk of the substituent. Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)CRCR)(CO)_9$ yields the corresponding $H_3Ru_3(\mu_3\text{-}CCHRCH_2R)(CO)_9$.

The implication of methylene coupling as a mechanism of chain growth in the metal suface-catalyzed Fischer–Tropsch (F–T) reaction has stimulated investigations of the chemistry of polynuclear alkylidene and alkylidyne complexes.[1,2] A number of examples of coupling between alkylidene ligands and unsaturated hydrocarbons on metal complexes have been reported.[3,4] A few examples of carbon–carbon bond formation between alkylidyne ligands and unsaturated hydrocarbons have also been reported,[5] and studies of hydrocarbons adsorbed on metal sufaces have identified alkylidyne fragments.[6] Mononuclear alkylidyne complexes react reversibly with alkynes to form metallacyclobutadienes,[7] while dibridged 1,3-dimetalloallyl moieties are produced from dimetallic alkylidynes.[5]

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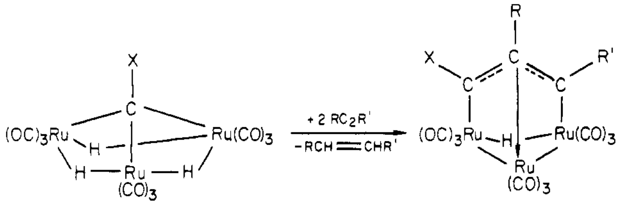
Coupling of diphenylacetylene and methylene on a triosmium cluster generates a triply bridging 1,3-dimetalloallyl (eq 1).[4] The relevance of these coupling reactions

$$\mathrm{Os_3(\mu\text{-}CH_2)(C_2Ph_2)(CO)_9} \rightarrow \mathrm{HOs_3(\mu_3\text{-}\eta^3\text{-}CHCPhCPh)(CO)_9} \quad (1)$$

to processes occurring on metal surfaces has yet to be demonstrated, but if these systems are to prove useful as models for surfaces,[8] systematic studies of reactivity and mechanism are necessary. We have recently utilized the methylidyne cluster series $H_3M_3(\mu_3\text{-}CX)(CO)_9$ (M = Ru, Os; X = H, Me, Ph, CO_2Me, Cl, Br, OMe)[9–12] for reactivity studies of hydrogen elimination,[13] alkene hydrogenation,[14] and ligand substitution.[15] We report here reactions of these clusters with alkynes that result in alkylidyne–alkyne coupling and further hydrogenation of the coupled products to generate new alkylidyne clusters.

The clusters $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe,[11] Ph,[10] Me[9]) react with an excess of alkyne C_2R_2 at room temperature to generate the corresponding $C_2H_2R_2$[16] and clusters formulated as $HRu_3(\mu_3\text{-}\eta^3\text{-}CXCRCR)(CO)_9$ (**1**, X = OMe, R = Me; **2**, X = OMe, R = H; **3**, X = OMe, R = Ph; **4**, X = R = Ph; **5**, X = R = Me) (eq 2) in yields of 15–70% after chromatography; also formed are cyclotrimerized alkyne products and a number of uncharacterized metal-containing products in low yield. When X = OMe, a significant side-product is $HRu_3(\mu\text{-}COMe)(CO)_{10}$;[11,17] however, at higher temperatures (60–70 °C) **1–3** can be formed from $HRu_3(\mu\text{-}COMe)(CO)_{10}$ and the appropriate alkyne.



(2)

These 1,3-dimetalloallyl clusters are derivatives of clusters previously prepared via reactions of $Ru_3(CO)_{12}$ with alkenes, dienes, or alkynes.[18] Some of these have been characterized by X-ray crystallography,[18b,19] as well as by spectroscopic methods. Related iron[20] and osmium[4,21] clusters have also been prepared. Thus, comparison of the spectroscopic properties of clusters **1–5** with derivatives whose structures have previously been established leaves no doubt as to the characterization of these compounds. In each instance the mass spectrum displays the molecular ion and ions resulting from stepwise loss of nine carbonyls. The IR spectra[22] of **1–5** are very similar to those reported for other $HRu_3(\mu_3\text{-}\eta^3\text{-}C_3R_3)(CO)_9$ clusters.[18] The ^{1}H NMR spectra[22] are particularly useful; coupling of 2 Hz is found between the allylic hydrogen in the 2-position and the hydride ligand, while no coupling is noted between the hydride and the allylic hydrogen in the 1-position. As was reported for $HRu_3(\mu_3\text{-}\eta^3\text{-}CHCHCMe)(CO)_9$,[18e] the coupling constant between adjacent allylic hydrogens of **2** is 7.5 Hz.

The two possible isomers arising from reactions of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ with terminal alkynes are readily distinguished by ^{1}H NMR spectroscopy.[22] Both isomers $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)CHCR)(CO)_9$ (**6**, R = Ph; **8**, R = *n*-Bu) and $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)CRCH)(CO)_9$ (**7**, R = Ph; **9**, R = *n*-Bu) in a roughly 2:1 ratio, respectively, are products from reactions with phenylacetylene and 1-hexyne. However, only $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)CHCCMe_3)(CO)_9$ (**10**) is formed with 3,3-dimethyl-1-butyne, implying that the regiochemistry is determined by steric interactions. Isomers **8** and **9**, easily separated by chromatography, do not interconvert at temperatures below the point of decomposition, and no exchange with added alkyne has been observed. Thus, the products are kinetically, rather than thermodynamically, determined.

The mechanism of alkyne–methylidyne coupling is currently under investigation, but some preliminary proposals can be made. The relative reactivities of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ toward alkynes parallel those found for substitution by $AsPh_3$[15] (X = OMe ≫ Me > Ph), implying that CO dissociation is the rate-limiting step. Hydrogen transfer to alkyne probably precedes carbon–carbon coupling since **2** and other derivatives can be prepared from $HRu_3(\mu\text{-}COMe)(CO)_{10}$. Reactions of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ with alkenes in the presence of excess 1,3-cyclohexadiene produce 1 equiv of alkane and $HRu_3(\mu_3\text{-}CX)(CO)_8(1,3\text{-}C_6H_8)$,[14] and a plausible intermediate in the alkyne reaction is $HRu_3(\mu_3\text{-}CX)(CO)_9$(alkyne). The related formation of $HOs_3(\mu_3\text{-}\eta^3\text{-}CHCPhCPh)(CO)_9$ from $Os_3(CH_2)(C_2Ph_2)(CO)_9$ was proposed to involve carbon–carbon bond formation prior to carbon–hydrogen bond cleavage;[4] our results suggest that initial carbon–hydrogen bond cleavage to form $HOs_3(CH)(C_2Ph_2)(CO)_9$ is also a possible pathway. However, 1,3-dimetalloallyls are *not* products from reactions of alkynes with the isoelectronic $Co_3(\mu_3\text{-}CX)(CO)_9$ clusters,[23] and we have thus far been unable to prepare 1,3-dimetalloallyls from the μ-methylidynes $HFe_3(\mu\text{-}COMe)(CO)_{10}$[24] and $HRu_3(\mu\text{-}CNR_2)(CO)_{10}$.[11,25] Clearly the

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(16) The only olefinic product detected after reaction of 2-decyne with $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ was *cis*-2-decene (ca. 60% yield, determined by ^{1}H NMR). Cluster products were $HRu_3(\mu\text{-}COMe)(CO)_{10}$ and the two isomers $HRu_3(\mu_3\text{-}\eta^3\text{-}C(OMe)C_2(Me)(C_7H_{15}))(CO)_9$.

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(22) Representative spectral data. **1**: mass spectrum, *m/e* 656 (^{102}Ru$_3$); IR(C_6H_{12}) 2092 (m), 2064 (vs), 2040 (vs), 2023 (s), 2010 (sh), 2004 (s), 1989 (w), 1972 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 6.01 (s, 3 H), 7.11 (s, 3 H), 7.92 (s, 3 H), 29.47 (s, 1 H). **2**: mass spectrum, *m/e* 628 (^{102}Ru$_3$); IR (C_6H_{12}) 2099 (w), 2074 (s), 2043 (s), 2031 (m), 2021 (m), 2014 (m), 2007 (w), 1994 (w), 1970 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 1.56 (d, 1 H_A), 3.25 (dd, 1 H_B), 6.19 (s, 3 H), 29.98 (d, 1 H_C), J_{AB} = 7.5 Hz, J_{BC} = 2.4 Hz. **11**: mass spectrum, *m/e* 658 (^{102}Ru$_3$); IR(C_6H_{12}) 2077 (vs), 2032 (vs), 2015 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 5.94 (m, 2 H_A), 8.21 (m, 2 H_B), 8.98 (s, 9 H), 27.49 (s, 3 H), J_{AB} = 8.2 Hz.

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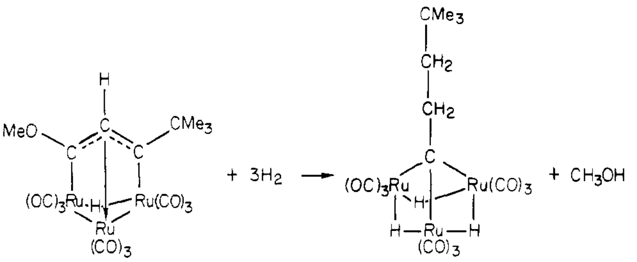
influences of the methylidyne substituent and the metal upon this reaction remain to be determined.

Reductive cleavage of the allyl moieties from the isomers $HRu_3(\mu_3\text{-}\eta^3\text{-}CXCHCR)(CO)_9$ and $HRu_3(\mu_3\text{-}CXCRCH)(CO)_9$ would give rise to linear and methyl-branched alkanes, respectively, which are the predominant alkane products of the F–T reaction. Therefore, we were interested in the reactivity of these molecules toward molecular hydrogen. In refluxing cyclohexane **10** is hydrogenated (1 atm, 4 h) to the alkylidyne cluster $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ (**11**)[22] in 30% yield (eq 3). Similarly, hydrogenation of **4** (4 atm, 18 h, 90 °C) and **6** (1 atm, 14 h, refluxing cyclohexane) gives the corresponding $H_3Ru_3(\mu_3\text{-}CCHRCH_2R')(CO)_9$ (**12**, R = R′ = Ph, 42% yield; **13**, R = H, R′ = Ph, 25% yield). Under more vigorous conditions we[11] and others[26] have shown that reductive cleavage of μ_3-alkylidynes can be induced; reactions of **11–13** with alkynes should allow further growth of the hydrocarbon chain. Studies to identify the mechanism of alkyne–alkylidyne coupling and to determine the reactivity of the 1,3-dimetalloallyl moiety are in progress.



(3)

Acknowledgment. This work has been supported by grants from the National Science Foundation (No. CHE 812 1059) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **1**, 86409-36-1; **2**, 86409-37-2; **3**, 86409-38-3; **4**, 86409-39-4; **5**, 86409-40-7; **6**, 86409-41-8; **7**, 86409-42-9; **8**, 86409-43-0; **9**, 86409-44-1; **10**, 86409-45-2; **11**, 86409-46-3; **12**, 86409-47-4; **13**, 86409-48-5; $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$, 71562-47-5; $H_3Ru_3(\mu_3\text{-}CPh)(CO)_9$, 73746-99-3; $H_3Ru_3(\mu_3\text{-}CMe)(CO)_9$, 40810-15-9; C_2Me_2, 503-17-3; C_2H_2, 74-86-2; C_2Ph_2, 501-65-5; $HRu_3(\mu\text{-}COMe)(CO)_{10}$, 71737-42-3; Ru, 7440-18-8; 1-hexyne, 693-02-7; phenylacetylene, 536-74-3; 3,3-dimethyl-1-butyne, 917-92-0.

Supplementary Material Available: Infrared, ^1H NMR, and mass spectral data for compounds **1–13** (2 pages). Ordering information is given on any current masthead page.

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Book Reviews

Advances in Organometallic Chemistry. Volume 21. Edited by F. G. A. Stone and R. West. Academic Press, New York. 1982. vi + 304 pp. $52.00.

Volume 21 of this well-established series maintains the high standards of earlier volumes and continues the tradition of covering a broad spectrum of topics within both transition-metal and main-group organometallic chemistry.

Although electrophilic aromatic substitution reactions provide the classic routes to complexes containing functionalized cyclopentadienyl ligands, only a relatively narrow range of complexes undergo these reactions. This has led to the development of a number of other synthetic routes to functionalized complexes, and the first article in this volume, by Macomber, Hart, and Rausch, reviews these alternative routes. The survey is organized according to the nature of the functionalized group attached to the cyclopentadienyl ligand and is restricted, unfortunately, to relatively reactive functional groups such as carbonyls, halogens, and alkenyls. Simple alkyl, aryl, and silyl substituents have been excluded, but the article does include a brief review of the preparation of polymer-bound complexes.

The article on metalloboranes by Housecroft and Fehlner is a well-organized and thoughtful review of the recent (1975–mid 1981) literature. The review is partly descriptive, presenting and classifying the known metalloboranes, but its main value lies in the analogies drawn between metalloboranes and other classes of organometallics. Their relationship to metallocarboranes is only mentioned briefly, but the analogies between individual borane ligands and the isoelectronic hydrocarbons are developed at some length and examined critically. Most interestingly, perhaps, there is a lucid introduction to the cluster model for metalloboranes and a balanced discussion of the differences between those metalloboranes that are best described as metal complexes containing borane ligands and those whose structures and properties require that they be discussed as heterometalloclusters.

Darensbourg's review of ligand substitution processes in metal carbonyls is a particularly timely contribution. It was for many years assumed that substitutions of two electron ligands in organotransition-metal complexes were relatively straightforward processes, which could be largely rationalized in terms of a sequence of 16- and 18-electron intermediates. Recent detailed work on a number of systems, however (facilitated in part by the application of isotopic labelling techniques), has shown that substitution reactions occur by a range of mechanisms and are frequently controlled by subtle factors. This review concentrates on one system, octahedral metal carbonyl complexes, and provides a well-integrated account of recent developments in their substitution chemistry. A particularly attractive feature is the extensive use which is made of the Langford and Gray classification of substitution processes.

The article on 1,4-diaza-1,3-butadiene (α-diimine) ligands by van Koten and Vrieze is perhaps the most specialized of those presented in this volume. The α-diimine skeleton is best known in the 2,2′-bipyridine and phenanthroline ligands, but there is also an extensive chemistry of acyclic α-diimines. The authors have been major contributors to this area, and they present a comprehensive and detailed review of acyclic α-diimines beginning with ligand and complex synthesis. There are extensive discussions of the solid-state structures of the ligands and complexes and of the diverse bonding modes exhibited. There is a separate section on metal 1,4-diaza-1,3-butadiene radicals and their ESR spectroscopy. The last section on chemical activation of the coordinated ligands provides a detailed and critical account of the reported reaction chemistry of the systems.

The final article in this volume describes the chemistry of multiply bonded Ge species and is again a comprehensive review of an area by one of the major contributors. Satgé takes evident pleasure in pointing out that materials containing multiple bonds to Ge were classified, until recently, as nonexistent compounds, and then writes a review (with over 100 references) of species containing double bonds from Ge to C, O, S, N, P, Ge, Bi, and other metals. The material is organized according to the nature of the atom bonded to Ge. Since most of the species mentioned are reactive intermediates or are, at best, of limited stability, there is an emphasis on decomposition reactions and on trapping reactions.

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