CpMn(CO)$_3$ and CpRe(CO)$_3$ solutes in both liquid crystals.

Ligand Exchange in Tetraalkylaluminate Ions: Catalysis by the Sodium Ion

Naseer Ahmad, Frank K. Cartledge,* M. C. Day,* and James H. Medley

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received October 20, 1983

When NaAlMe$_4$ and NaAlEt$_4$ are combined in benzene solution containing HMPA, exchanges of alkyl groups occur resulting in a statistical distribution of alkylaluminate ions. Rates of exchange can be followed by ^{27}Al heteronuclear decoupled ^{1}H NMR, and pseudo-first-order rate constants are a function of HMPA to Na$^+$ mole ratio, decreasing to essentially zero in pure HMPA. The reactions are interpreted as occurring in contact ion pairs in which two aluminate anions occupy coordination sites on the same Na$^+$. A large decrease in exchange rate occurring at HMPA:Na$^+$ = 2.5:1 is proposed to be due to the formation of solvent-bridged species of stoichiometry [2Na·5HMPA]$^{2+}$.

Mixed alkyl derivatives of the group 3 elements are of considerable interest for synthetic and other purposes.[1] While mixed alkylboranes are stable toward disproportionation under a variety of conditions,[1] trialkylaluminum derivatives are well-known to give rapid intermolecular alkyl group exchange. Mixed organoborates of types MBR$_3$R'[2] and MBR$_3$H[3] have been known for some time and are apparently perfectly stable. The situation with respect to mixed aluminates containing H and alkyl groups is less clear,[4,5] and mixed alkyl compounds of the type MAlR$_n$R'$_{4-n}$ are apparently unknown in pure form. A previous attempt to prepare such species in our laboratories by mixing an alkyllithium reagent and a trialkylaluminum in benzene resulted in a mixture containing LiAlR$_4$, LiAlR$_3$R', LiAlR$_2$R'$_2$, LiAlRR'$_3$, and LiAlR'$_4$.[6]

Results and Discussion

Exchange Equilibria. Anticipating that exchange pathways available to LiAlR$_4$ salts would not necessarily be the same as those available to the Na analogues, we have investigated the exchange reactions occurring on mixing NaAlMe$_4$ and NaAlEt$_4$ in benzene in the presence of controlled amounts of HMPA or Me$_2$SO. Combining these components results in a two-liquid-phase system with all of the organometallic, and essentially all of the donor solvent, in the lower phase. Many properties of these two-phase mixtures have been described elsewhere.[7] In the lower phase, alkyl group exchange does take place, and the progress of the exchange can be followed by ^{27}Al heteronuclear decoupled ^{1}H NMR, as shown in Figure 1. The spectrum of the equilibrated mixture shows four methyl proton signals that are almost base line resolved at 100 MHz and that appear in 1:3:3:1 relative intensities when the salts are mixed in a 1:1 molar ratio. The distribution of Me groups among the four Me-containing species is thus a random one; i.e., $\Delta H°$ for eq 1 is 0, and $\Delta S°$ is determined only by the contribution of external symmetry numbers to the partition coefficients.[8]

$$3NaAlMe_4 + 3NaAlEt_4 \rightleftharpoons$$
$$2NaAlMe_3Et + 2NaAlMe_2Et_2 + 2NaAlMeEt_3 \quad (1)$$
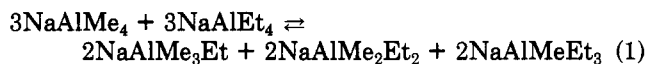
Exchange of hydrogen or alkyl groups in aluminate species has been observed by others. In some solvents a slow H–H or H–D exchange can be observed in the ^{27}Al NMR of solutions of MAlH$_4$ and MAlD$_4$.[9] Since there is considerable overlapping of the ^{27}Al signals, the proportions of LiAlH$_n$D$_{4-n}$ species present cannot be determined, but the inference is drawn that all five possibilities are formed when LiAlH$_4$ and LiAlD$_4$ are mixed in 1:1 ratio and that the final equilibrium distribution is random. In contrast, in exchanges observed between MAlH$_4$ and MAlR$_4$ in THF, catalyzed by AlR$_3$, the formation of mixed MAlH$_n$R$_{4-n}$ species does not follow a random pattern.[5] For instance, a 1:1 mixture of NaAlH$_4$ and NaAlMe$_4$ in THF at 66 °C (presumably with AlMe$_3$ catalysis) results in formation of NaAlH$_2$Me$_2$ exclusively, as indicated by the ^{27}Al NMR spectrum. The authors conclude that MAlH$_3$R

(1) Kulkarni, S. U.; Basaviah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212–4.

(2) Schlesinger, H. I.; Brown, H. C. *J. Am. Chem. Soc.* **1940**, *62*, 3429. Wittig, G.; Raff, P. *Justus Liebigs Ann. Chem.* **1951**, *573*, 195.

(3) Wittig, G.; Keicher, G.; Ruckert, A.; Raff, P. *Justus Liebigs Ann. Chem.* **1949**, *563*, 110. Brown, H. C.; Schlesinger, M. I.; Sheft, I.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 192. Honeycutt, J. B., Jr.; Riddle, J. M. *Ibid.* **1961**, *83*, 369.

(4) Westmoreland, T. D.; Bhacca, N. S.; Wander, J. D.; Day, M. C. *J. Organomet. Chem.* **1972**, *38*, 1.

(5) Gavrilenko, V. V.; Vinnikova, M. I.; Antonovich, V. A.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 2367–9.

(6) Ahmad, N.; Day, M. C., unpublished studies.

(7) (a) Medley, J. H.; Mooberry, E. S.; Day, M. C. *Can. J. Chem.* **1983**, *61*, 558–561. (b) Day, M. C.; Medley, J. H.; Ahmad, N. *Ibid.* **1983**, *61*, 1719–1721. (c) Medley, J. H. Ph.D. Dissertation, Louisiana State University, 1983.

(8) Stearn, A. E. *J. Am. Chem. Soc.* **1940**, *62*, 1630. Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; pp 1–3.

(9) Nöth, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 117. Nöth, H.; Rurländer, R.; Wolfgardt, P. *Ibid.* **1981**, *36B*, 31.
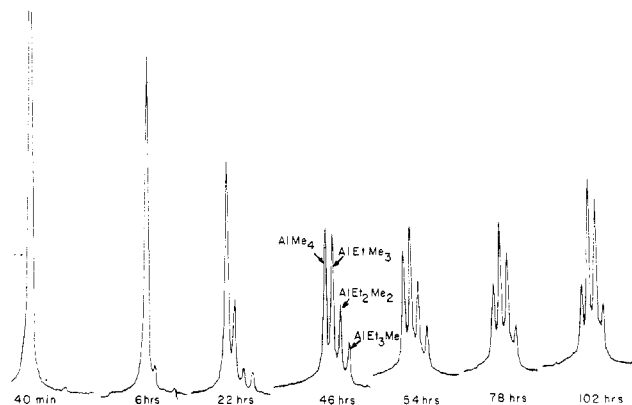
Figure 1. ^{27}Al decoupled ^{1}H NMR spectra in the region for methyl protons during exchange involving NaAlMe$_4$ and NaAlEt$_4$ mixed in a 1:1 ratio in benzene–HMPA.

species are unstable and dissociate into MAlH$_4$ and MAlH$_2$R$_2$. It is not clear why MAlHR$_3$, which is apparently stable, is not seen in the 1:1 NaAlH$_4$/NaAlR$_4$ mixtures. In our cases involving Me–Et exchange, some of all four Me-containing species can be seen even when the mole ratio of NaAlMe$_4$:NaAlEt$_4$ is 1:10.

Kinetic Approach to Equilibrium. The exchanges in the presence of HMPA and Me$_2$SO show many similarities. The detailed work reported below involved HMPA. Kinetics for the exchange process can be followed most accurately and conveniently by observing the disappearance of the ^{1}H NMR signal for AlMe$_4^-$. Due to the nature of the two-phase system, however, there are experimental restrictions on the variables which can ordinarily be altered. The starting ratios of AlMe$_4^-$:AlEt$_4^-$ can be varied, but the overall concentration of AlR$_4^-$ in the lower layer is essentially fixed. That concentration varies somewhat as the ratio of HMPA to salt is varied, but there are several lines of evidence to indicate that the natures of the species present in the lower phase are different with different HMPA to salt ratios. Hence, the standard kinetic experiment in which the concentrations of reagents are varied in order to determine a reaction order cannot be carried out with the present system. Within the experimental limitations, however, some significant kinetic work is possible.

We have modeled the progress of the reaction by computer, using the two mechanistic schemes which we consider most reasonable. In any mechanistic model there will be a large number of individual steps involving the five observable AlR$_n$R$'_{4-n}^-$ species, as well as any proposed intermediate species. One simplifying assumption made in the kinetic modeling was that for species of a particular kind, i.e., AlR$_4^-$ or AlR$_3$ or R$^-$, reactivity is independent of the electronic or steric nature of R; that is, that statistical contributions to $\Delta S^\ddagger$ are the only contributors to $\Delta G^\ddagger$. Thus, in cases of bimolecular steps, relative rate constants are assumed to be determined only by the products of the external symmetry numbers of the reactants.

The simpler of the two models involves bimolecular collisions of two AlR$_n$R$'_{4-n}^-$ which result in the exchange of an R for an R' in each of the two species. There are 12 distinguishable bimolecular exchange reactions (six equilibria such as that shown in eq 2) contributing to the

$$AlMe_4^- + AlEt_4^- \rightleftharpoons AlMe_3Et^- + AlMeEt_3^- \quad (2)$$

approach to the overall equilibrium position. When AlMe$_4^-$ and AlEt$_4^-$ are mixed in a 1:10 molar ratio, the model predicts a linear dependence of log [AlMe$_4^-$] on time over
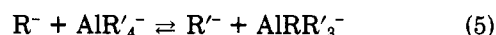
Table I. Rate Constants for Decay of NaAlMe$_4$ in Benzene-HMPA Solutions Containing an Initial 1:10 Molar Ratio of NaAlMe$_4$ to NaAlEt$_4$

HMPA:Na$^+$	k_{obsd}, min^{-1}	$k_2 = k_{obsd}/$ [NaAlEt$_4$], M^{-1} min^{-1}
2.5	$< 2 \times 10^{-5}$	$< 2 \times 10^{-5}$
2.3	0.0017	0.0020 ± 0.0002^a
2.1	0.0061	0.0068 ± 0.0002
1.9	0.011	0.012 ± 0.002
1.7	0.016	0.017 ± 0.0005
1.5	0.022	0.020 ± 0.0008

^{a} Error is derived from the standard deviation of the slope in the kinetic plot.

the first 10% of the time required to reach equilibrium. That 10% time period corresponds to >90% of the change in concentration of AlMe$_4^-$. In fact, the observed consumption of AlMe$_4^-$ does follow the predicted straight line behavior with correlation coefficients in the linear plots between 0.96 and 0.995.[10] In terms of the model presented above, the interpretation is relatively simple. We are observing only the contribution of (2) in the early parts of the reaction with [AlEt$_4^-$] effectively constant. The pseudo-first-order rate constants corresponding to this interpretation are shown in Table I. The values vary with HMPA to salt ratio. The salt concentration in the lower phase varies from 0.96 to 1.2 M in the range of HMPA:Na of 2.3:1.5. When the pseudo-first-order rate constants are converted to second-order rate constants corresponding to the forward reaction in (2), the reactivity is still dependent on the HMPA to salt ratio.

Any realistic mechanistic model other than that described above will be substantially more complex. We have considered the case in which the following equilibria contribute:

$$AlR_4^- \rightleftharpoons AlR_3 + R^- \quad (3)$$

$$AlR_3 + AlR'_4^- \rightleftharpoons AlR_2R' + AlRR'_3^- \quad (4)$$

$$R^- + AlR'_4^- \rightleftharpoons R'^- + AlRR'_3^- \quad (5)$$

Exchange reactions of both types 4 and 5 are known.[11]

Taking into account all AlR$_n$R$'_{4-n}^-$, AlR$_n$R$'_{3-n}$, R$^-$, and R$'^-$ species, there are eight equilibria of type 3, 12 equilibria of type 4, and four equilibria of type 5 for a total of 48 rate constants. Again the assumption is made that within each reaction type, relative rates are determined only by statistical factors. In this model, however, in addition to statistical factors, one must estimate the magnitudes of the equilibrium constants of type 3 and the rates of the reactions of types 4 and 5 relative to one another and relative to the rates of 3. The fact that no evidence is seen for the presence of AlR$_3$ and NaR in solutions of NaAlR$_4$ requires that the equilibrium constants of type 3 be very small, but the other magnitudes are a matter of guesswork. Our initial sets of choices for the rate constants did not lead to a model that reproduced the experimental findings. Specifically, the model predicted the correct equilibrium concentrations of the four Me-containing NaAlR$_n$R$'_{4-n}$ species but did not predict a linear plot of log [AlMe$_4^-$] vs.

(10) The aluminate salts are, of course, extremely air and moisture sensitive. Every effort was made, however, to prepare samples free of impurities in an Ar-filled drybox. Some error is expected in the measured area for the NaAlMe$_4$ peak, since it is not completely resolved from that for NaAlMe$_3$Et.

(11) Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134. Kieft, R. L.; Brown, T. L. *J. Organomet. Chem.* **1974**, *77*, 289–98. Watkins, J. J.; Ashby, E. C. *Inorg. Chem.* **1977**, *16*, 2075–81. Brown, C. A. *J. Organomet. Chem.* **1978**, *156*, C17–C19.

time in the initial time period following mixing of $AlMe_4^-$ and $AlEt_4^-$ in a 1:10 molar ratio. However, further manipulation of the rate constants did lead to such a prediction when the rate constants for type 4 reactions are slower by factors of 10–100 compared to the reverse of reaction 3 and faster by approximately a factor of 2 compared to the reactions of type 5. There is nothing intrinsically unreasonable about the set of rate constants that does reproduce experiment, and hence the kinetic modeling does not afford a clear choice among the mechanistic pathways. The meanings of the rate constants in Table I are somewhat different if the second model is the correct one. The period of linearity in decay of $[AlMe_4^-]$ does not necessarily correspond to one reaction exclusively, but mainly the two reactions below, with the first being faster than the second. The second-order rate constants noted in Table I would not have meaning under such conditions.

$$AlMe_4^- + AlEt_3 \rightarrow AlMe_3Et^- + AlMeEt_2$$

$$AlMe_4^- + Et^- \rightarrow AlMe_3Et^- + Me^-$$
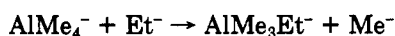
For several reasons we prefer the mechanistic interpretation involving bimolecular collision of AlR_4^- species. The first reason is that no evidence of the presence of RNa in solutions of $NaAlR_4$ has been put forward, even in much more polar solvents than benzene. Secondly, in our system the exchange essentially stops at ratios of HMPA to sodium ion greater than 2.5.[12] The latter observation does not seem consonant with the participation of AlR_3 or $(AlR_3)_2$ in the exchange process. In separate experiments we have investigated the HMPA dependence of the rate of exchange between $NaAlEt_4$ and $(AlMe_3)_2$ in benzene. Exchange reaches completion in less than 5 min even with a $HMPA:AlMe_3:NaAlEt_4$ ratio of 5:1:1; i.e., conditions under which both Na^+ ion[13] and $AlMe_3$[14] are coordinatively saturated with respect to HMPA. If dissociation of $NaAlR_4$ into RNa and AlR_3 were important in our system, then added HMPA should have the effect of increasing the amount of such dissociation, and since exchange continues unabated when $HMPA·AlMe_3$ is the principal species present in solution, we should expect no falloff in exchange rate to near zero with $HMPA:NaAlR_4$ ratios >2.5.

The previously reported exchange processes involving $LiBH_4/LiBD_4$,[15,16] $NaBH_4/NaBD_4$,[16] and $LiAlH_4/LiAlD_4$[9] are solvent dependent with exchange apparently occurring most slowly in the presence of solvents capable of cation solvation. These reports, along with our own observations, lead us to propose that a common mechanism for exchange involves mediation by the alkali-metal cation when exchange involves MR_4^- species. Such a suggestion involving $Li^+(AlH_4^-)_2$ triple ions has been made by Nöth for the case of $LiAlH_4$ exchange.[9] The precise form of the mediation by the cation probably varies depending upon the specific species and their degrees of aggregation in the medium. For our case of $NaAlR_4/NaAlR'_4$ exchange, we will present a somewhat more specific proposal below. The only obvious exception to cation mediation that we can find in the literature is the report that KBH_4 does show slow exchange with KBD_4 in 18-crown-6/$CHCl_3$,[16] conditions under which the K^+ ion would be expected to be coordinated and unable to participate in the exchange mechanism.

In the crystal structure of $NaAlEt_4$ the Na^+ ion is closely associated with the α-carbon of an ethyl group.[17] The Na-α-carbon distance is 2.7–2.8 Å, which is somewhat longer than the metal–carbon distance in the corresponding Li salt. In solution in solvents which do not strongly coordinate the Na^+ ion, it is reasonable to propose that the association of Na with the α-carbon still exists. We have previously observed changes in the proton NMR spectra of $NaAlEt_4$–benzene–HMPA solutions at a HMPA:salt ratio of 4, which we have interpreted as the point at which contact ion pairs have been completely converted into solvent-separated ion pairs.[13] At lower ratios of HMPA to salt, Na^+-AlR_4^- contact ion pairs and aggregates are assumed to be present. Recent work involving measurement of ^{23}Na NMR relaxation times as a function of HMPA:Na^+ ratio has led us to propose a stepwise increase in the number of HMPA molecules in the solvation shell of Na^+ ion as HMPA is added, up to a maximum of four.[7a] We suggest that the Na^+ cation is able to catalyze exchange of alkyl groups between two AlR_4^- anions when there are at least two vacant coordination sites on Na, as shown in eq 6. The species shown

$$S = HMPA$$
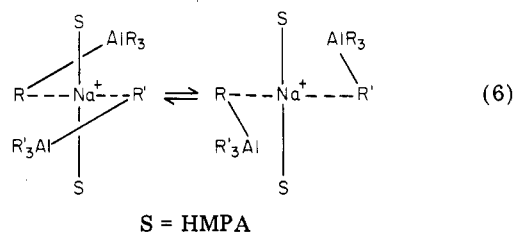
in (6) are not necessarily proposed to be triple ions which exist discretely in solution. Rather, the species participating in the alkyl group exchanges could be complex aggregates of which only a portion is represented in (6). Our proposal would lead to the expectation that the rate of exchange would diminish as the ratio of HMPA:Na^+ ion approaches 3. In fact, the exchange essentially ceases at a ratio of 2.5. Indeed, the HMPA:Na^+ ratio of 2.5 represents something of a magic number in the present system, with several properties reaching a maximum or a minimum, including a maximum in viscosity of the lower phase at 30°, minima in activation energy for ionic mobility and ^{27}Al line width, and at least approximate inflection points in equivalent conductance and volume of the lower phase. We cannot give specific interpretations to all these phenomena, but clearly there is some significant transition. We suggest that three of the four coordination sites on the Na^+ ion are effectively occupied at HMPA:Na^+ = 2.5 through the formation of a solvent-bridged species of stoichiometry $[2Na·5HMPA]^{2+}$ (I). At this point large aggregates are effectively broken up, as two AlR_4^- anions cannot be in the coordination sphere of one Na^+ ion.

I
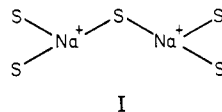
Preliminary studies have been carried out by using Me_2SO as the donor. Exchange rates diminish rapidly at $Me_2SO:Na^+$ ratios greater than 4:1 and essentially cease at 4.5:1. Me_2SO is a weaker donor than HMPA toward Na^+.[7b] It is also possible that the coordination number of Na^+ is greater with Me_2SO than with HMPA. In any

(12) Between ratios of 2.3 and 2.5 the rate of exchange decreases by a factor of at least 100.

(13) Ahmad, N.; Day, M. C. *J. Am. Chem. Soc.* 1977, *99*, 941.

(14) Pasynkiewicz, S.; Buczkowski, Z. *J. Organomet. Chem.* 1970, *22*, 525–35.

(15) Smith, B. E.; James, B. D.; Peachey, R. M. *Inorg. Chem.* 1977, *16*, 2057–62.

(16) Oxton, I. A.; McInnes, A. G.; Walter, J. A. *Can. J. Chem.* 1979, *57*, 503–5.

(17) Medley, J. H.; Fronczek, F. R.; Ahmad, N.; Day, M. C.; Rogers, R. D.; Kerr, C. R.; Atwood, J. L., submitted for publication in *J. Cryst. Spect. Res.*

event, the phenomenon of decreasing exchange rate associated with the addition of a relatively good donor toward Na$^+$ is observed with both Me$_2$SO and HMPA, although at this time less is known about the details of solvation of Na$^+$ by Me$_2$SO.

The implications of our proposals for the preparation of mixed aluminates are significant. In the case of MAlH$_4$/MAl(alkyl)$_4$ mixtures,[5] exchange rates are insignificant in THF alone but become appreciable on addition of Al(alkyl)$_3$. Hydride exchange in LiAlH$_4$ has been proposed in the case involving toluene/THF as solvent (THF:LiAlH$_4$ = 2:1) but not in pure THF.[9] We observe alkyl exchange rates which are a function of HMPA:NaAlR$_4$ ratio. Clearly the best possibility for preparation of stable mixed aluminates, whether containing H or alkyl groups will be under conditions where there is maximum coordination of the cation. Other evidence from our laboratories indicates that the best commonly available donor toward Na$^+$ is HMPA. It may be possible to control the rates of a wide variety of organometallic exchange processes by making use of the excellent coordinating ability of HMPA. Indeed, the (AlMe$_3$)$_2$/NaAlEt$_4$ exchange, which is immeasurably fast in benzene, even after some HMPA is added, is very much slower in pure HMPA as solvent.

Experimental Section

Sodium tetraethylaluminate was prepared by a previously reported procedure.[18] Sodium tetramethylaluminate was prepared by adding 0.2 mol of trimethylaluminum dropwise to 0.2 mol of sodium dispersion in 250 mL of toluene and refluxing for 3 h under argon. The mixture was allowed to cool, and the black product was separated by filtration through a fine sintered glass

funnel and washed with toluene and hexane. The sodium tetramethylaluminate dissolved on stirring with ether, and the solution was filtered through a sintered glass funnel. The solution was concentrated by evaporation of the solvent and NaAlMe$_4$ precipitated by adding toluene. This process of dissolution in ether and precipitation with the addition of toluene was repeated twice. Finally the solid white NaAlMe$_4$ was obtained by evaporation of ether under vacuum. Both sodium tetramethylaluminate and tetraethylaluminate are highly sensitive to atmospheric oxygen and moisture, and hence all operations were performed under an argon atmosphere or in an argon atmosphere drybox.

Kinetic Runs. Benzene was refluxed for 24 h over calcium hydride prior to distillation under a nitrogen atmosphere onto sodium wire. HMPA was refluxed for 48 h over calcium hydride at approximately 0.5 torr prior to distillation. The solutions were prepared in the drybox by weighing the salts in separate containers and adding weighed amounts of HMPA followed by dilution with benzene. The solutions were mixed, and the zero time was noted. The solution separated into two phases immediately. The NMR tube was filled with the lower phase, closed with a pressure cap, taken out of the box, and quenched in liquid nitrogen. The ^{1}H NMR spectra were run at various time intervals on a Varian HA100 spectrometer equipped with a ^{27}Al decoupler. The peaks were cut out, and the area under the NaAlMe$_4$ peak was normalized with respect to the total area of the peaks in this region (including the peaks for NaAlMe$_3$Et, NaAlMe$_2$Et$_2$, and NaAlMeEt$_3$). Spectra were recorded at several HMPA:Na ratios. The insolubility of NaAlMe$_4$ at lower HMPA concentrations precludes the kinetic studies below a HMPA:Na$^+$ ratio of 1.0.

(18) Frey, F. W., Jr.; Kobetz, P.; Robinson, G. C.; Sistruck, T. O. *J. Org. Chem.* **1961**, *26*, 2950.

Acetylene Additions to Saturated and Unsaturated Clusters: Four-Electron Addition with and without CO Loss

Shane A. MacLaughlin, Nicholas J. Taylor, and Arthur J. Carty*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The unsaturated cluster (μ-H)Ru$_3$(CO)$_9$(μ-PPh$_2$) reacts with diphenylacetylene affording a 1:1 adduct, (μ-H)Ru$_3$(CO)$_9$(μ_3-η^2-PhC≡CPh)(μ-PPh$_2$), without CO displacement. Crystals are triclinic of space group P$\overline{1}$ with a = 9.616 (2) Å, b = 14.194 (4) Å, c = 15.218 (4) Å, α = 102.17 (2)°, β = 102.31 (2)°, γ = 97.91 (2)°, and Z = 2. X-ray analysis based on 2744 observed ($I \geq 3\sigma(I)$) reflections and refinement to R = 0.030 and R_w = 0.034 has revealed that the product is a 50-electron cluster with an open triangular framework, μ-hydrido and μ-phosphido bridges, and face-capping μ_3-acetylene. This reaction is thus an example of four-electron addition without CO loss. The saturated cluster Ru$_5$(CO)$_{13}$(μ_4-η^2-C≡CPh)(μ-PPh$_2$) also reacts readily to yield a 1:1 complex of formula Ru$_5$(CO)$_{12}$(μ_5-η^2-C≡CPh)(μ_3-η^2-PhC≡CC≡CPh)(μ-PPh$_2$) with diphenylbutadiyne. An X-ray structure determination (monoclinic crystals of space group P2$_1$/n with a = 11.195 (1) Å, b = 25.638 (3) Å, c = 16.384 (2) Å, β = 92.79 (1)°, Z = 4, R = 0.030, R_w = 0.035 on 4275 reflections) has shown that the acetylene caps an open triangular face as a four-electron ligand. In this case four-electron addition results in Ru–Ru bond cleavage and loss of a single carbonyl group.

Introduction

The intrinsically high reactivity associated with electronic and coordinative deficiency in mononuclear complexes suggests that unsaturated transition-metal clusters should exhibit unique patterns of chemical behavior with potential applications to catalysis.[1] In addition however,

reaction modes are accessible to clusters that have no counterparts in mononuclear chemistry. Of particular

(1) For recent work on coordinatively unsaturated cluster chemistry see: (a) Kulzick, M.; Price, T.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 1256. (b) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878. (c) Fryzuk, M. D. *Organometallics* **1982**, *1*, 408.