

Fluxional Molecular A-Frames Containing Bridging Acetylide Ligands. Synthesis of $[\text{Rh}_2(\mu-\eta^2\text{-C}_2\text{R})(\text{CO})_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]\text{ClO}_4$ ($\text{R} = \text{H}, \text{Ph}, t\text{-Bu}$) and Their Reactions with Nucleophiles

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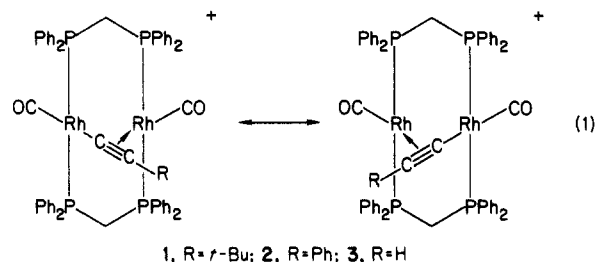
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Summary: The carboxylate A-frame complexes $[\text{Rh}_2(\mu\text{-O}_2\text{CR}^1)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{R}^1 = \text{CH}_3, \text{CF}_3$) react with terminal acetylenes, RC_2H ($\text{R} = \text{H}, \text{Ph}, t\text{-Bu}$ ($\text{R}^1 = \text{CF}_3$ only)), to give the $\mu\text{-}\eta^2\text{-acetylide}$ complexes $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ in which the acetylide ligand is fluxional, exhibiting an oscillatory type motion. The acetylide groups in these complexes are susceptible to nucleophilic attack by H^- and PR_3 to give, in the case of H^- , unstable bridging vinylidene complexes $[\text{Rh}_2(\mu\text{-C}=\text{CHR})(\text{CO})_2(\mu\text{-dppm})_2]$. In solution, the *tert*-butylvinylidene complex undergoes an unprecedented reoxidation to the parent acetylide complex.

Owing to the difficulties inherent in the characterization of chemisorbed species,¹ a great deal of attention is currently being focussed on detailing the structure and chemical reactivity of hydrocarbon fragments bound to polynuclear transition-metal complexes, in the belief that such compounds should function as reasonable models for their chemisorbed counterparts as well as displaying unusual patterns of reactivity. This interest has recently spawned numerous articles reviewing aspects of this approach from differing perspectives.¹⁻¹⁰ Acetylide complexes^{9,10} have not escaped this attention, although only Carty and co-workers seem to have had any success at elaborating the chemistry of acetylide ligands in polynuclear complexes.^{10,11} The vast majority of acetylide complexes investigated by Carty's group are coordinatively saturated and hence the reactivity of the acetylide has been limited to (albeit novel) nucleophilic attack at either the α - or the β -carbon of the acetylenic linkage, except in the reaction of the unsaturated cluster $\text{Ru}_3(\text{CO})_8(\text{PPh}_2)(\text{C}\equiv\text{C}-t\text{-Bu})$ with dihydrogen in which partial hydrogenation of the acetylide function was observed. In this communication we wish to report the synthesis of a series of $\mu\text{-}\eta^2\text{-acetylide}$ complexes $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) in which the acetylide groups span two unsaturated metal centers.¹² These complexes are unique in that the acetylide functions oscillate rapidly in their mode of attachment to the metals and undergo β -hydride addition to generate vinylidene

complexes. In the case of $\text{R} = t\text{-Bu}$, the addition of hydride is reversible.

We recently reported the synthesis of the complex $[\text{Rh}_2(\mu\text{-}\eta^2\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ¹³ which suggested to us that isoelectronic acetylide complexes should also be accessible. This and our observation that the carboxylate complexes $[\text{Rh}_2(\mu\text{-O}_2\text{CR}^1)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{R}^1 = \text{CF}_3, \text{CH}_3$) react with H_2/CO mixtures to yield $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$,¹⁴ prompted us to attempt the reaction of terminal acetylenes with these carboxylates. Accordingly, the action of excess acetylene, RC_2H , on $[\text{Rh}_2(\mu\text{-O}_2\text{CR}^1)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ in dichloromethane solution led to isolation of the complexes $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (1, $\text{R} = t\text{-Bu}$;¹⁵ 2, $\text{R} = \text{Ph}$;¹⁶ 3, $\text{R} = \text{H}$ ¹⁷) from diethyl ether. The spectroscopic properties of 1-3, including an X-ray crystallographic analysis of 1,¹⁸ clearly establish these compounds as further examples of molecular A-frames. Of particular note is the fact that all three exhibit typical AA'A''XX' patterns in the ³¹P NMR spectra, establishing that there is a rapid oscillation of the acetylide group between the metal atoms (eq 1) as is also observed for the cyanide ligand in the



complexes $[\text{Rh}_2(\mu\text{-}\eta^2\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$,¹³ $(\text{NEt}_4)[\text{Cp}_2\text{Mo}_2(\mu\text{-}\eta^2\text{-CN})(\text{CO})_3]$,¹⁹ and $[\text{Mn}_2\text{H}(\mu\text{-CN})(\text{CO})_4(\mu\text{-dppm})_2]$.²⁰ As in the first of these examples, the motion of the acetylide groups in 1-3 was still rapid at -80°C .

Compounds 1-3 mimic the behavior of the cation $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2]^+$ ²¹ by forming labile CO and SO_2 adducts $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{R})(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{L} = \text{CO}, \text{SO}_2$). More interesting, however, is the behavior of the acetylide complexes toward nucleophiles. Despite the cationic nature of the complexes, we have found nu-

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(15) 1: 4.5 h, $\text{R}^1 = \text{CF}_3$; red or orange crystals, 77%; $\Delta_M(\text{acetone}) = 131 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$; IR (cm^{-1} , CH_2Cl_2) 1996 (sh), 1982 (vs) ($\nu(\text{CO})$), 2023 (mw) ($\nu(\text{C}\equiv\text{C})$); ¹H NMR (CD_2Cl_2) δ 7.53 (m, Ph), 4.25, 3.66 (m, CH_2), 0.47 (s, *t*-Bu); ³¹P NMR (relative to 85% H_3PO_4 , external, CD_2Cl_2) δ 20.47 (m, ¹ $J_{\text{Rh-P}}$ + ² $J_{\text{Rh-P}}$ = 113.7 Hz). Anal. Calcd for $\text{C}_{58}\text{H}_{53}\text{P}_4\text{O}_6\text{ClRh}_2$: C, 57.52; H, 4.41; P, 10.23. Found: C, 57.22; H, 4.43; P, 11.05.

(16) 2: 3.5 h, $\text{R}^1 = \text{CH}_3$, red needles, 86%; $\Delta_M(\text{acetone}) = 122 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$; IR (cm^{-1} , CH_2Cl_2) 1998 (sh), 1983 (vs) ($\nu(\text{CO})$), 2019 (mw) ($\nu(\text{C}\equiv\text{C})$); ¹H NMR (CD_2Cl_2) δ 7.34 (m, Ph), 6.68 (m, C_2Ph), 4.26, 3.48 (m, CH_2); ³¹P NMR (relative to 85% H_3PO_4 , external, CD_2Cl_2) δ 20.79 (m, ¹ $J_{\text{Rh-P}}$ + ² $J_{\text{Rh-P}}$ = 113.0 Hz). Anal. Calcd for $\text{C}_{54}\text{H}_{45}\text{P}_4\text{O}_6\text{ClRh}_2$: C, 58.53; H, 4.01; P, 10.06. Found: C, 57.95; H, 4.06; P, 9.83.

(17) 3: 1 h; $\text{R}^1 = \text{CH}_3$, red-orange crystals, 74%; $\Delta_M(\text{acetone}) = 127 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$; IR (cm^{-1} , CH_2Cl_2) 2010 (s), 1986 (vs) ($\nu(\text{CO})$), 1886 (mw) ($\nu(\text{C}\equiv\text{C})$), confirmed by ¹³CO labeling studies), 3216 (mw) ($\nu(\text{CH})$); ¹H NMR (CD_2Cl_2) δ 7.43 (m, Ph), 4.28, 3.46 (m, CH_2), 5.60 ((acetone-*d*₆) s, CH_2Cl_2); ³¹P NMR (-40°C , relative to 85% H_3PO_4 , external, CD_2Cl_2) δ 19.24 (m, ¹ $J_{\text{Rh-P}}$ + ² $J_{\text{Rh-P}}$ = 113.4 Hz). Anal. Calcd for $\text{C}_{54}\text{H}_{45}\text{P}_4\text{O}_6\text{Cl}_2\text{Rh}_2$: C, 54.61; H, 3.79; P, 10.35. Found (CH_2Cl_2 hemisolvate): C, 54.28; H, 3.75; P, 10.02.

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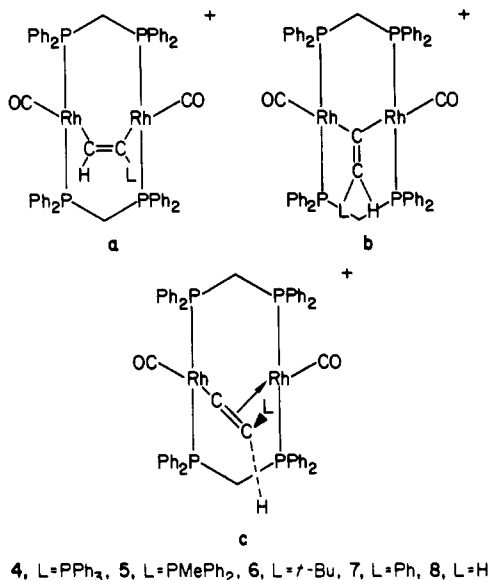
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 (12) During the preparation of this manuscript, a report detailing the synthesis of a $\mu\text{-}\eta^2\text{-acetylide}$ complex of a mixed platinum/rhodium dimer appeared. Hutton, A. T.; Shebanzadeh, B.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* 1984, 549.

cleophilic addition to compounds 1–3 to be a considerably less general phenomenon than observed for their closest analogue $\text{Fe}_2(\mu\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_6$.¹⁰ Furthermore, we have found no clear cut evidence in favor of α -attack in our system. The apparently decreased incidence of nucleophilic addition to the acetylide function in 1–3 is in part due to the fact that the metal centers now also compete favorably as a site for attack.²²

Steric factors are undoubtedly another important factor in determining the outcome of nucleophilic attack on 1–3. Thus, for example, neither 1 nor 2 are subject to attack by tertiary phosphines whereas 3 reacts with excess PR_3 to give adducts $[\text{Rh}_2(\mu\text{-C}_2\text{H}(\text{PR}_3))(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($\text{R} = \text{Ph}$, 4; $\text{R}_3 = \text{MePh}_2$, 5)²³ which could possess any of the structural types depicted in a–c, depending on whether



α - or β -addition has occurred. Although we cannot assign structures for these compounds unambiguously, our evidence suggests that the structure of type b is most likely the correct one. Molecular models suggest somewhat severe steric crowding in a and c (impossibly so in c) between the phosphine addend and the dppm phenyl and methylene groups, which is absent in b. Furthermore, the $^{31}\text{P}\{\text{H}\}$ NMR spectra for 4 and 5 in the dppm region appear as slightly perturbed AA'A''XX' patterns coupled with a further $I = 1/2$ nucleus.²⁴ This suggests that the added phosphorus nucleus is coupling almost equivalently with

all four dppm phosphorus atoms, a situation not likely to pertain in a structure such as a. Although there are undoubtedly electronic effects at play, we feel that steric effects also play a dominant role in preventing adduct formation between the bulky phosphorus nucleophiles and complexes 1 and 2, a possibility which has been alluded to previously.¹⁰

$[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{-}t\text{-Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ reacts with either $\text{Li}[\text{BHEt}_3]$ or NaBH_4 in ethanol suspension to yield an air-sensitive, intensely colored bridging vinylidene complex $\text{Rh}_2(\mu\text{-C}_2[\text{H}]\text{-}t\text{-Bu})(\text{CO})_2(\mu\text{-dppm})_2$ (6).²⁵ Analogous derivatives of 2 (7) and 3 (8) were prepared in situ by the addition of $\text{Li}[\text{BHEt}_3]$.²⁵ The structures of 6–8 are almost certainly of type b resulting from β -addition to the acetylide. The possibility of α -addition to give complexes of type a has been eliminated by noting that under these conditions, 7 and 8 would be identical with the acetylene complexes $\text{Rh}_2(\mu\text{-}\eta^2\text{-HC}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2$, previously characterized by Eisenberg et al.²⁶ Their physical properties are, however, quite different. Structures of type c can be eliminated on steric grounds, at least for 6 and 7 (vide supra). The observation of an AA'A''XX' pattern in the ^{31}P NMR spectrum of 8 does not allow us to distinguish between a structure of type b or fluxional c. The close similarity of 8 to 6 and 7 would suggest, however, a symmetric $\mu\text{-}\eta^1$ -bridging mode for the vinylidene ligand in all three complexes.

It seems most likely that the initial attack of $[\text{BHEt}_3]^-$ occurs directly at a metal center, although the possibility exists that initial attack occurs at a terminal carbonyl to produce a transient formyl species.²⁷ A rapid hydride migration from [formyl to] metal to C_β would then complete the transformation. The implication that vinylidene formation here results from the transfer of a metal hydride to C_β of the bound acetylide is consistent with the thesis that acetylene to vinylidene rearrangements on metal clusters occur via initial oxidative addition of the acetylene followed by hydride migration to yield the vinylidene tautomer.²⁹ A recent communication has also noted the addition of a platinum hydride $[\text{PtH}(\text{acetone})(\text{PEt}_3)_2]^+$, across the $\text{C}\equiv\text{C}$ bond of an acetylide ligand in $\text{Pt}(\text{C}_2\text{Ph})_2(\text{PEt}_3)_2$ to generate a bridging vinylidene complex.³⁰

All three vinylidene complexes are unstable in air, especially in solution. Compounds 7 and 8 undergo oxidation to yield as yet uncharacterized materials containing terminal and bridging carbonyl groups. In dichloromethane solution, however, 6 undergoes a novel and unprecedented

(25) 6: blue crystals, 97%; $\Lambda_M(\text{acetone}) = 0 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$; IR (cm^{-1} , CH_2Cl_2) 1943 (s), 1918 (vs) ($\nu(\text{CO})$), 1666 (w) ($\nu(\text{C}\equiv\text{C})$, tentative only, Nujol); ^1H NMR (CD_2Cl_2) δ 7.31 (m, Ph), 4.60 (m, vinylidene H), 2.95, 3.75 (m, CH_2), 0.41 (s, *t*-Bu); ^{31}P NMR (relative to H_3PO_4 , external, CD_2Cl_2) δ 30.13 (m). Anal. Calcd for $\text{C}_{58}\text{H}_{54}\text{P}_4\text{O}_2\text{Rh}_2$: C, 62.60; H, 4.89. Found: C, 61.75; H, 4.90. 7: purple; IR (cm^{-1}) 1948 (s), 1924 (vs); ^{31}P NMR δ 29.53 (m). 8: blue; IR (cm^{-1}) 1945 (s), 1923 (vs); ^{31}P NMR (-40°C) δ 30.99 (m, [$^1J_{\text{Rh-P}} + ^2J_{\text{Rh-P}}$] = 167.9 Hz). ^1H NMR spectra of 7 and 8 were rendered uninterpretable by excess Et_3BH^- anion, BEt_3 derivatives and THF. The vinylidene proton resonance in 12 was verified by deuteration.

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(27) Bulky $[\text{BHEt}_3]^-$ attacks all three acetylide complexes with comparable facility, unlike similarly bulky phosphines. Molecular modeling suggests severe steric interactions will occur between the BHEt_3^- anion and dppm phenyl groups during either direct C_β attack or attack at either Rh atom from either face. Such interactions are exacerbated by the acetylide R group, especially when $\text{R} = t\text{-Bu}$. Direct attack at a terminal carbonyl group is slightly less hindered. The addition of $[\text{BHEt}_3]^-$ to cationic carbonyls is known to generate formyl complexes, the less stable of which are themselves capable of functioning as hydride donors.²⁸

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(22) For example, 2 and 3 react on mixing with 1 equiv of *p*-tolyl isocyanide to give products resulting from carbonyl substitution. We see no evidence for nucleophilic addition to the acetylide function as observed for $\text{M}_2(\mu\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_6$. E.g., $\text{R} = \text{Ph}$: IR (cm^{-1} , CH_2Cl_2) 2112 (s) ($\nu(\text{CN})$), 1981 (vs) ($\nu(\text{CO})$). A slight shoulder on the high-energy side of the $\nu(\text{CO})$ absorption was attributed to $\nu(\text{C}\equiv\text{C})$. $\text{R} = \text{H}$: IR (cm^{-1}) 2115 (s) ($\nu(\text{CN})$), 1987 (vs) ($\nu(\text{CO})$), 1873 (mw) ($\nu(\text{C}\equiv\text{C})$). The $\nu(\text{CN})$ frequencies in these isocyanide complexes are in the range expected for terminal RNC ligands and too low to be diagnostic of an isocyanide bound to an acetylide ligand. See ref 10, pp 122–3.

(23) 4: purple crystals, 75%; IR (cm^{-1} , CH_2Cl_2) 1973 (s), 1957 (vs); ^{31}P NMR (relative to 85% H_3PO_4 , external, CD_2Cl_2 , excess PR_3) δ 24.29 (m, (dppm)), -11.8 (m, ($\text{C}_2[\text{H}]\text{PPh}_2$)), -4.76 (s, br (PPh_3 , free)). Anal. Calcd for $\text{C}_{72}\text{H}_{80}\text{P}_5\text{O}_8\text{ClRh}_2$: C, 61.01; H, 4.27; P, 10.93. Found: C, 60.61; H, 4.19; P, 11.20. 5: purple crystals, 71%; IR (cm^{-1} , CH_2Cl_2) 1974 (s), 1956 (vs); ^{31}P NMR δ 27.66 (m, (dppm)), -14.5 (m, ($\text{C}_2[\text{H}]\text{PMePh}_2$)), -24.8 (s, br (PMePh_2 , free)). Anal. Calcd for $\text{C}_{67}\text{H}_{56}\text{P}_5\text{O}_8\text{ClRh}_2$: C, 59.38; H, 4.31; P, 11.43. Found: C, 58.34; H, 4.38; P, 11.55.

(24) The perturbation is manifested by a lifting of degeneracy in the minor peaks of the dppm multiplets. The principal lines of the multiplets (singlets in an AA'A''XX' pattern) appear as doublets with separations of 7.20 Hz for 4 and ca. 5.5 Hz for 5. Furthermore, these lines also showed the beginnings of structure to the extent that in 5, the higher field principal absorption appeared as a doublet of doublets at high resolution, with further splittings of ca. 1.0 Hz.

reoxidation to the parent cation $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{-}t\text{-Bu})(\text{CO})_2(\mu\text{-dppm})_2]^+$ with a concomitant color change from blue to red.³¹ The reoxidation is clean, no other products being discernible. We have been able to eliminate the possibility that the vinylidene complex **6** undergoes oxidation by functioning as a hydride donor to adventitious water. Whether in wet or dry degassed CH_2Cl_2 , **6** remains intact until sufficient dry dioxygen is admitted, after which the oxidation proceeds smoothly and rapidly. We are currently attempting to determine the stoichiometry of the oxidation as well as identifying the nature of the dioxygen reduction products.

To us, the most intriguing aspect of this oxidation process concerns whether the interaction of **6** with dioxygen occurs initially at one or both metal centers or whether dioxygen attack occurs directly at the ligand, possibly through some form of electron-transfer process. Our attempts to discern the exact nature of this initial interaction are ongoing.

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Registry No. 1, 94294-51-6; 2, 94323-95-2; 3, 94294-53-8; 4, 94294-55-0; 5, 94294-57-2; 6, 94294-58-3; 7, 94294-59-4; 8, 94294-60-7; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{Bu-}t)(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94294-62-9; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94294-64-1; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94294-66-3; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{Bu-}t)(\mu\text{-SO}_2)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94323-97-4; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-SO}_2)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94323-99-6; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{H})(\mu\text{-SO}_2)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 94324-01-3; $[\text{Rh}_2(\mu\text{-}\eta^2\text{-C}_2\text{Bu-}t)(\text{CO})_2(\mu\text{-dppm})_2]^+$, 94294-50-5; $[\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 93646-75-4; $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$, 93646-77-6; $t\text{-BuC}_2\text{H}$, 917-92-0; PhC_2H , 536-74-3; HC_2H , 74-86-2.

(31) In the $\nu(\text{CO})$ region of the infrared, this transformation is characterized by the gradual but complete disappearance of bands at 1943 and 1918 with the concomitant growth of bands at 2022 (w), 1996, and 1982 cm^{-1} over a period of ca. 30 min. Further monitoring up to 24 h shows no further changes.

A Stable 16-Electron Rhodium(III) Rhodacarborane Derived from an Intermediate Containing an Agostic Hydrogen Atom. Molecular Structure of *closo*-3-($\eta^3\text{-C}_8\text{H}_{13}$)-1,2-(CH_3)₂-3,1,2-RhC₂B₉H₉

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Summary: Protonation of $[\text{PPN}][\text{closo}\text{-}3,3\text{-}(\eta^4\text{-}1,5\text{-cyclooctadiene})\text{-}1,2\text{-}(\text{CH}_3)_2\text{-}3,1,2\text{-RhC}_2\text{B}_9\text{H}_9]$ with trifluoroacetic acid in dichloromethane at -73°C results in the formation of an unstable intermediate that exhibits an agostic hydrogen interaction and that rearranges at 7°C to produce an unusually stable 16-electron rhodium(III) metallacarborane, *closo*-3-($\eta^3\text{-C}_8\text{H}_{13}$)-1,2-(CH_3)₂-3,1,2-RhC₂B₉H₉, which, as determined from an X-ray crystal structure study, is not stabilized via any apparent M-H-C interactions.

The importance of the formation of transient 16-electron metal species in organometallic catalytic reactions has been widely recognized for a great many years, and attention has recently focused upon the ability of such unsaturated transition metal species to activate aliphatic C-H bonds of both coordinated and uncoordinated organic moieties.¹ There have now been several reported examples of stable 16-electron transition-metal complexes containing organic ligands whose stability has been attributed to a unique mode of interaction between the metal center and a proximal C-H bond of the bound ligand; the C-H bond shares its σ electrons with the metal to provide a two-electron, three-center M-H-C interaction, thus providing the metal with a formal 18-electron configuration.² We wish to report here the formation of a surprisingly stable, 16-electron rhodium(III) (η^3 -cyclooctenyl)rhodacarborane species that is unusual in that, unlike other electron-deficient η^3 -cycloalkenyl organotransition-metal complexes,² it exhibits no apparent distortion of the cyclooctenyl or carborane ligands due to M-H-C interactions, yet its formation occurs via an intermediate that appears to contain such an M-H-C interaction. We also wish to report evidence which indicates that the stability of the (η^3 -cyclooctenyl)rhodacarborane appears to be due to the substituents on the carbon atoms of the carborane ligand.

Protonation in vacuo of a dichloromethane solution of the (1,5-cyclooctadiene)rhodacarborane anion $[\text{closo}\text{-}3,3\text{-}(\eta^4\text{-}1,5\text{-cyclooctadiene})\text{-}1,2\text{-}(\text{CH}_3)_2\text{-}3,1,2\text{-RhC}_2\text{B}_9\text{H}_9]^- (1)^3$ using 2 equiv of trifluoroacetic acid at -73°C was found to result in the formation of a thermally unstable intermediate, **1a**, which exhibits broad resonances in the 200-MHz ^1H FT NMR spectrum at 3.99, 2.95, 2.31, 2.08, and -3.94 ppm. The unusual resonance at -3.94 ppm was found to represent a single proton via integration. Due to the broadness of the signals, combined with a lack of response to decoupling, it appears that this unstable species is fluxional in solution. By comparison of the ^1H NMR spectrum for **1a** with that of complex **1**,⁴ the resonances at 3.99, 2.31, and 2.08 ppm can be attributed to vinyl, methylene, and carboranyl methyl protons, respectively, and based upon chemical shift, the resonance at 2.95 ppm appears to be representative of aliphatic protons. However, the broad upfield resonance observed at -3.94 ppm was not readily identifiable. In order to determine the nature of this unique proton, we chose to examine potential sites of interaction between complex **1** and the acid source.

Since a chemical shift of -3.94 ppm is not unusual for a hydrogen involved in a bridging B-H-B bonding interaction, the possibility that the protonation of **1** occurs at the carborane ligand to produce an exo-nido species⁵ containing a B-H-B bridging bond was considered. Examination of this protonation reaction via low-temperature 127-MHz $^{11}\text{B}\{^1\text{H}\}$ FT NMR spectroscopy ruled out this possibility by revealing only resonances due to an apparently symmetric (six resonances) *closo*-metallacarborane species and displaying no signals due to boron atoms involved in either B-H-B or M-H-B bonding interactions.⁶

(1) Janowicz, A. H.; Bergman, R. *J. Am. Chem. Soc.* 1983, 105, 3929 and references therein.

(2) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395 and references therein.

(3) Analytically pure complex **1** was prepared by reaction of the disubstituted monoanion $\text{Cs}[\text{nido}\text{-}7,8\text{-}(\text{CH}_3)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ with 4 equiv of sodium isopropoxide and 1 equiv of $[\text{Rh}(1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ in 2-propanol, followed by precipitation of the PPN^+ salt by addition of $(\text{PPN})\text{Cl}$.

(4) **1**: ^1H NMR (CD_2Cl_2 , 25°C , δ) 3.95 (s, br, 4 H, vinylic CH), 2.38 (m, br, 8 H, methylene CH), 2.08 (s, 6 H, carboranyl methyl CH).

(5) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 2979.