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Molecular A-Frames. Reversible Addition of Diazoalkanes to Dinuclear Metal Centers and the Formation of $[Rh_2(\mu\text{-}N_2CRCO_2Et)(CO)_2(dppm)_2]$ (R = H, CO_2Et)†

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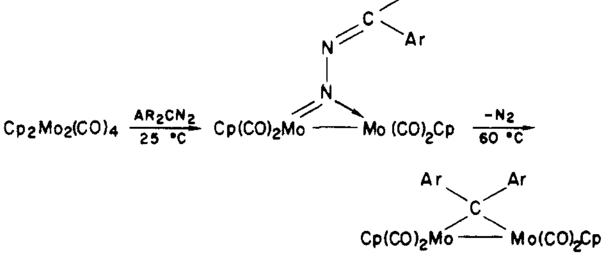
Ethyl diazoacetate and diethyl diazomalonate react with the A-frame precursor complex $[Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2]$ where dppm = bis(diphenylphosphino)methane resulting in the elimination of H_2 and formation of 1:1 adducts. These new complexes are formulated as the A-frame molecules $[Rh_2(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2]$ and $[Rh_2(\mu\text{-}N_2C(CO_2Et)_2)(CO)_2(dppm)_2]$ based on elemental analyses, spectroscopic data, and subsequent reaction chemistry. On photolysis or thermolysis, these adducts do not eliminate N_2 but rather dissociate the intact diazoalkane molecule. The ethyl diazoacetate adduct is reversibly protonated to form $[Rh_2(\mu\text{-}N_2CH_2CO_2Et)(CO)_2(dppm)_2]BF_4$ on treatment with $HBF_4\cdot OEt_2$ whereas the diethyl diazomalonate derivative reacts with this same protic source to effect loss of the diazoalkane and formation of $[Rh_2(\mu\text{-}H)(CO)_2(dppm)_2]BF_4$. The A-frame complex $[Rh_2(\mu\text{-}p\text{-}N_2C_6H_4NO_2)(CO)_2(dppm)_2]PF_6$ is prepared by the reaction of $(p\text{-}N_2C_6H_4NO_2)PF_6$ with the A-frame precursor complex.

Introduction

In the past several years, diazoalkanes have been used extensively in the preparation of μ-alkylidene complexes.[1] These complexes are of interest because of their possible relationship to organometallic species involved in methylene transfer reactions and in catalysis of the Fischer–Tropsch reaction and olefin metathesis.[2] However, relatively little is known about the actual reaction pathway leading to (μ-alkylidene)metal complex formation from diazoalkanes, and in only a few instances stable diazoalkane complexes have been isolated and structurally characterized.

In 1980, Curtis reported the reaction of $(\eta\text{-}C_5H_5)_2Mo_2(CO)_4$ with diaryldiazomethanes that results in the formation of air-stable green diazoalkane adducts.[3] Thermal decomposition of these adducts (60 °C in benzene) leads to N_2 extrusion and μ-diarylcarbene complexes as shown in eq 1. Recently, Herrmann has reported that the closely related dialkyldiazomethane complexes contain unsymmetrically bridging diazo ligands.[4] Heating these complexes leads to cleavage fo the N–N bond and, in most cases, formation of a symmetrically bridged imine ligand as well as a terminal isocyanate ligand, as shown in eq 2.



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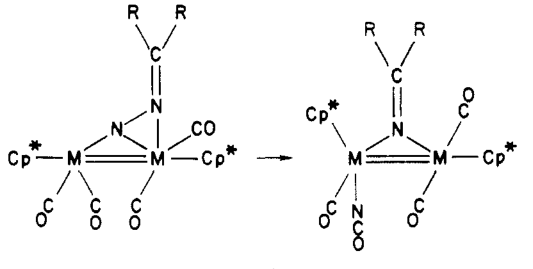

(2)

M=Mo, W; Cp*=Me5C5

Another example of diazoalkane complex formation was reported in 1981 by Shapley and co-workers who described the reaction of diazomethane with the cluster $Os_3(CO)_9(PhC{\equiv}CPh)$.[5] This reaction, shown in eq 3, proceeds

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† This paper is dedicated to the memory of Earl L. Muetterties, a gifted and imaginative scientist and a warm and caring friend.

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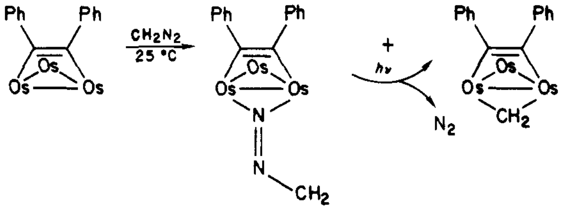
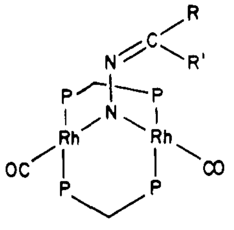
cleanly to yield nearly equal amounts of a thermally stable μ-diazomethane adduct and a μ-methylene complex. The μ-diazomethane species can be efficiently converted to the μ-methylene complex upon photolysis.



(3)

We describe herein the formation of new μ-diazoalkane adducts, A, which are based on the A-frame structure.[6]



A

These complexes do not eliminate N_2 either thermally or photochemically to form the corresponding μ-alkylidene species nor do the diazoalkane ligands undergo N–N bond cleavage. Instead, the diazoalkane ligand in these complexes dissociates intact, and substitution occurs readily. In the case of the ethyl diazoacetate adduct, reversible protonation of the diazoalkane ligand occurs without N_2 loss or decomposition.

Experimental Section

Reagents. Rhodium trichloride hydrate (Johnson Matthey), bis(diphenylphosphino)methane, dppm (Strem), sodium borohydride (J. T. Baker), tetrafluoroboric acid–diethyl ether complex (Aldrich), ethyl diazoacetate (Aldrich), p-nitrobenzenediazonium hexafluorophosphate (Aldrich), and gases H_2 and CO (Matheson CP) were used as purchased. Tetrahydrofuran and benzene were dried by distilling from sodium/benzophenone. Toluene was distilled from sodium. Ethanol was distilled from magnesium turnings. $Me_2SO\text{-}d_6$ was dried by storing over molecular sieves in a drybox. Diethyl diazomalonate was prepared by a published procedure.[7]

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrophotometer calibrated with polystyrene film and cyclohexane solution. Samples were either solutions prepared under N_2 or Nujol mulls on NaCl plates. ^1H and ^{31}P NMR spectra were recorded on a Bruker WH-400 spectrometer at 400 and 162 MHz, respectively. Chemical shifts are reported in parts per million downfield of internal Me_4Si for ^1H and external 85% H_3PO_4 for ^{31}P. Samples were prepared on a high vacuum line and flame sealed under vacuum, except where stated.

Gases were analyzed on a Hewlett-Packard 5700A gas chromatograph with thermal conductivity detectors and helium carrier gas (40 mL/min). Gas samples (0.5 mL) were withdrawn from the reaction flask through septa using a gas-tight Pressure-Lok syringe. The following columns were used: 2 ft × $^1/_4$ in. 5A molecular sieves for N_2, H_2, and CO and 12 ft × $^1/_4$ in. Porapak Q for CO_2.

Conductance measurements were made on DMF solutions of the complexes under inert atmosphere utilizing a Barnstead DM-70CB conductivity bridge equipped with a Barnstead B-10 1.0-cm cell. A working cell constant was determined from the ratio of the observed specific conductance of 0.02 N aqueous KCl with the literature value of 0.002 768 Ω^{-1} cm^{-1} at 25 °C.[8] Typically, equivalent conductances for the complexes in solution were determined at five concentrations ranging from ca. 5 to 0.1 mM. The equivalent conductances at 1 mM were then determined from an Onsager plot of equivalent conductance vs. $(concentration)^{1/2}$. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of Complexes. All syntheses were routinely performed under an atmosphere of dry nitrogen with modified Schlenk techniques. $[Rh_2(CO)_3(dppm)_2]$, I, and $Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2$, II, were prepared by published procedures.[9,10]

$[Rh_2(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2]$, III. $[Rh_2H_2(CO)_2(dppm)_2]$ (II, 0.1 g, 0.097 mmol) was partially dissolved in 5 mL of THF under H_2 (1 atm). Ethyl diazoacetate (13 μL, 0.13 mmol) was added by syringe to the reaction solution. The reaction was stirred at room temperature for 2–3 h. The suspension clears forming a deep red solution from which the product was precipitated with ether and filtered under N_2. The precipitate was washed with ether and dried in vacuo; yield 0.085 g (76%). Anal. Calcd for $C_{56}H_{50}P_4O_4N_2Rh_2$: C, 56.96; H, 4.61; P, 10.49; N, 2.37. Found: C, 57.11; H, 4.54; P, 10.52; N, 2.18.

$Rh_2(\mu\text{-}N_2C(CO_2Et)_2)(CO)_2(dppm)_2$, IV. This complex was prepared by the same procedure given for III using 20 μL (0.13 mmol) of diethyl diazomalonate in place of ethyl diazoacetate. A purple solution forms from which the product was isolated as a deep purple precipitate; yield 0.094 g (80%). Anal. Calcd for $C_{59}H_{54}P_4O_6N_2Rh_2$: C, 58.23; H, 4.48; P, 10.18; N, 2.30. Found: C, 57.98; H, 4.79; P, 9.95; N, 2.22.

$[Rh_2(\mu\text{-}N_2CH_2CO_2Et)(CO)_2(dppm)_2]BF_4$, V. Complex III (0.06 g, 0.052 mmol) was suspended in 5 mL of absolute ethanol, and $HBF_4{\cdot}OEt_2$ (30 μL, 0.22 mmol) was added with a microliter syringe. The suspension clears momentarily followed by precipitation of an orange powder. The reaction was stirred for 30 min and filtered in air. The precipitate was washed with ether and dried in vacuo, yielding 0.06 g (94%) of analytically pure V. Anal. Calcd for $C_{56}H_{51}P_4O_4Rh_2BF_4$: C, 54.57; H, 4.11; P, 10.05. Found: C, 54.36; H, 4.32; P, 10.49. Equivalent conductance (DMF): 74 Ω^{-1} cm^2 mol^{-1} (lit. value (DMF) 65–90 for 1:1 electrolyte).

$[Rh_2(\mu\text{-}N_2C_6H_4NO_2)(CO)_2(dppm)_2]PF_6$, VI. Complex II (0.097 mmol) was partially dissolved in 5 mL of acetone under H_2. To this suspension was added $NO_2C_6H_4N_2PF_6$ (0.14 g, 0.475 mmol) in 10 mL of acetone. The resulting mixture was stirred for 1 h. The product was isolated as an orange powder after several recrystallizations from acetone/ether; yield 0.064 g (50%).

Photolyses. Photolyses were carried out in flame-sealed 5-mm ^1H NMR tubes using a Hanovia lamp no. 679A10, unfiltered, with the sample 15 cm away from the lamp.

Results and Discussion

Ethyl diazoacetate (EDA) and diethyl diazomalonate (DEDM) react with $[Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2]$, II, leading to the reductive elimination of H_2 and replacement of the hydride ligands by 1 equiv of substrate. The structures of these complexes are proposed as A-frames based on the spectroscopic data presented in Table I and elemental analyses. When either adduct $[Rh_2(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2]$, III, or $[Rh_2(\mu\text{-}N_2C(CO_2Et)_2)(CO)_2(dppm)_2]$, IV, is treated with CO, substitution of the μ-diazoalkane ligand occurs resulting in the formation of $[Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2]$, I, which has been characterized previously,[9] and liberation of free diazoalkane as detected by ^1H NMR spectroscopy. In addition, treating either adduct III or IV with borohydride leads to regeneration of the starting complex II. This contrasts with the $Rh_2(CO)_3(dppm)_2$, I, which does not react with BH_4^- to liberate CO and regenerate II. These observations indicate that in these

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Table I

	IR (Nujol) ν_{CO}, cm^{-1}	^{1}H NMR, δ			^{31}P NMR, δ
		phenyl region	methylene region	other	
$Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2$[8,9] (II)	1920	7.6 (s, 16 H), 6.9 (s, 24 H)	3.6 (s, 4 H)	−7.9 (t, 20 Hz, 2 H)[a]	39.3 (m)[b]
$Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2$[8] (I)	1945, 1930, 1830	7.5 (s, 16 H), 6.9 (s, 24 H),[a] 7.53 (16 H), 7.25 (8 H), 7.20 (16 H)[c]	4.2 (s, 4 H),[a] 4.46 (4 H)[c]		19.4 (m)[b]
$[Rh_2(\mu\text{-}H)(CO)_2(dppm)_2]BF_4$[8] (VII)	2000, 1050 ($\nu(BF_4)$)	7.7 (s, 16 H), 7.5 (t, 7 Hz, 8 H), 7.4 (t, 7 Hz, 16 H)[c]	4.6 (s, 4 H)[c]	−11.8 (m, 1 H)[c]	23.0 (m)[b]
$Rh_2(\mu\text{-}N_2CHCO_2Et)(CO)_2(dppm)_2$ (III)	1955, 1940, 1610 ($\nu(CO_2Et)$), 1400 ($\nu(N_2)$)	7.7 (8 H), 7.6 (8 H), 7.1 (8 H), 7.0 (4 H), 6.8 (4 H), 6.7 (8 H)[a]	3.4 (m, 2 H), 2.4 (m, 2 H)[a]	4.5 (q, 7 Hz, 2 H),[a] 1.4 (t, 7 Hz, 3 H), 5.4 (br s)[d,c]	20.0 (m)[c]
$Rh_2(\mu\text{-}N_2C(CO_2Et)_2(CO)_2(dppm)_2$ (IV)	1955, 1940, 1670, 1570 ($\nu(CO_2Et)$), 1380 ($\nu(N_2)$)	7.7 (8 H), 7.6 (8 H), 7.3 (16 H), 7.1 (8 H)[a]	3.3 (m, 2 H), 3.0 (m, 2 H)	3.5 (q, 7 Hz, 4 H),[a] 0.9 (t, 7 Hz, 6 H)	29.1 (m)[b]
$[Rh_2(\mu\text{-}N_2CH_2CO_2Et)(CO)_2(dppm)_2]BF_4$ (V)	1990, 1960, 1740 ($\nu(CO_2Et)$), 1050 ($\nu(BF_4)$)	7.9 (8 H), 7.7 (8 H), 7.5 (8 H), 7.4 (8 H), 7.3 (8 H)[a]	3.8 (m, 2 H), 3.2 (m, 2 H)[a]	4.5 (s, 2 H),[a] 3.9 (q 7 Hz, 2 H), 1.1 (t, 7 Hz, 3 H)	9.0 (m)[c]
$[Rh_2(\mu\text{-}N_2C_6H_4NO_2)(CO)_2(dppm)_2]PF_6$ (VI)	1990, 1960, 1480, 1340 ($\nu(NO_2)$), 850 ($\nu(PF_6)$)	8.2 (8 H), 7.6 (8 H), 7.5 (8 H), 7.3 (4 H), 7.1 (12 H)[a]	4.9 (m, 2 H), 3.8 (m, 2 H)[a]	7.8 (s br, 2 H),[a] 7.7 (s br, 2 H)	25.9 (m)[b]

[a] Benzene-d_6. [b] Dimethyl-d_6-sulfoxide. [c] Acetone-d_6. [d] This resonance is not observed in benzene-d_6.

A-frame complexes the μ-diazoalkane ligands coordinate to Rh more weakly than does the μ-carbonyl ligand in $Rh_2(CO)_3(dppm)_2$, I.

This conclusion is further demonstrated by the behavior of these adducts under photolysis or thermolysis conditions. Heating or photolyzing a benzene or acetone solution of III or IV leads to the formation of 0.5 equiv of the carbonyl adduct I, based on comparison of the ^{1}H NMR and IR spectra with those of authentic I. In addition, on heating or photolyzing III in a vacuum sealed NMR tube, ca. 0.10 equiv free EDA is detected in the ^{1}H NMR spectrum. The remaining EDA has decomposed in a similar manner to that observed in a control experiment in which a benzene solution of free EDA was photolyzed in the absence of metal complex. We see no evidence for the elimination of N_2 when either III or IV is heated or photolyzed under He and the gas phase above the reaction is monitored by GC.

The reactivity of the new diazoalkane adducts III and IV was further examined by using protic reagents. The complexes I, III, and IV exhibit markedly different reactivity with $HBF_4{\cdot}OEt_2$. In previous studies complex I was shown to form a μ-hydride–μ-carbonyl complex, $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$, VII, on treatment with $HBF_4{\cdot}OEt_2$.[9] However, when either 1 equiv or a large excess of $HBF_4{\cdot}OEt_2$ is added to a THF solution of III, protonation at the α-carbon of the diazoalkane ligand occurs to form $[Rh_2(\mu\text{-}N_2CH_2CO_2Et)(CO)_2(dppm)_2]BF_4$, V. As shown in Table I, a new resonance appears in the ^{1}H NMR spectrum at 4.5 ppm due to the α-protons in the diazo group. A triplet at 1.1 ppm and quartet at 3.9 ppm can be attributed to the ethyl group in V. Both resonances are shifted upfield of those in the parent complex III, which occur at 1.4 and 4.5 ppm, respectively. The remaining ^{1}H NMR resonances are due to the dppm ligand and are typical of A-frame type molecules. This protonation of III to form V is reversible as shown by regeneration of III upon addition of NaOEt to an ethanol slurry of V.

A complex analogous to the cationic species V is formed when II is treated with an aryldiazonium salt. The reaction of II with $(p\text{-}NO_2C_6H_4N_2)PF_6$ in acetone results in the evolution of H_2 and the formation of $[Rh_2(\mu\text{-}N_2C_6H_4NO_2)(CO)_2(dppm)_2]PF_6$, VI, as determined by the IR, ^{1}H NMR, and ^{31}P NMR data listed in Table I. In addition to the ^{1}H NMR resonances of the dppm ligands, resonances also appear at 7.8 and 7.7 ppm that can be attributed to the aromatic protons in the bridging diazo ligand. In addition, IR stretches at 1990 and 1960 cm^{-1} show the presence of terminal CO ligands, and stretches at 1480 and 1340 cm^{-1} are attributed to the nitro group. The stretch assignable to $\nu(PF_6)$ occurs at 850 cm^{-1}. The IR spectrum does not exhibit any band assignable to ν(NN) as was also the case reported for the similar complexes $[Pd_2(\mu\text{-}N_2Ar)Cl_2(dppm)_2]BF_4$[11] and $[Ir_2(\mu\text{-}N_2Ar)(\mu\text{-}O)(NO)_2(PPh_3)_2]$.[12]

The behavior of the diazomalonate complex IV with $HBF_4{\cdot}OEt_2$ differs from that just described for the acetate complex III. Complex IV reacts with $HBF_4{\cdot}OEt_2$ to effect loss of the bridging diazomalonate ligand and formation of the known μ-hydridic cationic complex $[Rh_2(\mu\text{-}H)(CO)_2(dppm)_2]BF_4$, VIII.[9] This complex is also formed when the parent complex II is treated with $HBF_4{\cdot}OEt_2$. The different reactivity of III and IV with $HBF_4{\cdot}OEt_2$ parallels the difference in stability of the free diazo ester compounds. Diethyl diazomalonate is more highly con-

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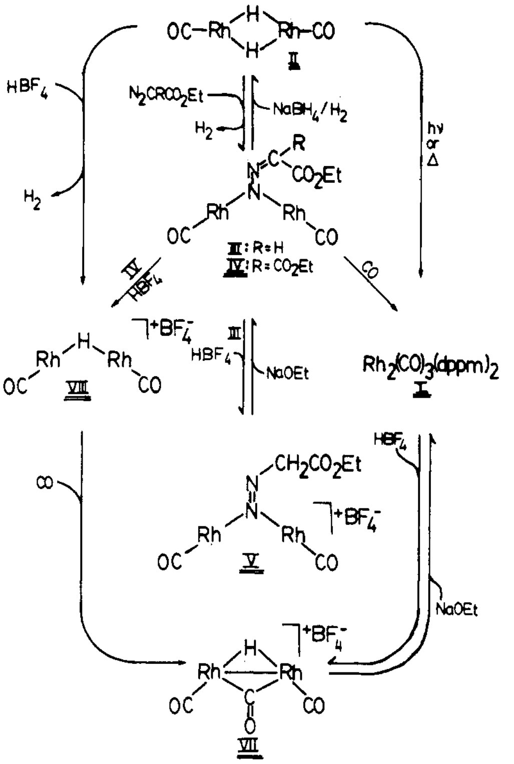
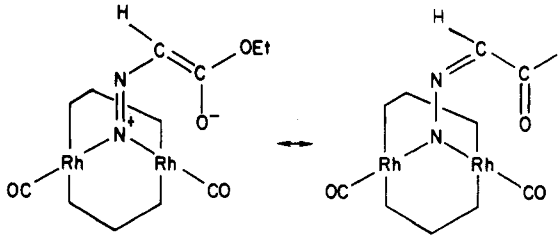
Scheme I



The dppm ligands are omitted for clarity.

jugated and more stable than ethyl diazoacetate and apparently more easily displaced from the A-frame molecule. The reactivity of these new diazo ester complexes is summarized in Scheme I.

The position of the ester carbonyl stretches in the IR spectra of complexes III, IV, and V provides additional information regarding the bonding in these complexes. The ester stretch appears at 1610 cm^{-1} for III, which is considerably lower in energy than the ester stretch of free EDA (1700 cm^{-1}). This lowering of energy may be attributed to the conjugative interaction shown as B. In addition, interaction between one of the rhodium centers and the ester carbonyl oxygen may also contribute to this lowering. A similar effect has been observed in a range of $HOs_3(CO)_{10}$(alkyl) complexes. For example, $HOs_3(CO)_{10}(CH(CO_2Et)CH_2CO_2Et)$ exhibits ester stretches at 1688 and 1615 cm^{-1} that are attributed to the uncoordinated and coordinated ester carbonyls, respectively.[13] In the present system, protonation of III to form V results in a shift in the ester carbonyl stretch from 1610 to 1740 cm^{-1} due to loss of both the conjugative interaction and any possible coordination by the ester carbonyl.



B

The behavior of these new bridged diazo ester complexes differs markedly from that previously reported for μ-diazoalkane complexes.[1,3-5] In the present systems, the highly stable nature of both I and the free diazoester compounds appears to outweigh the stability that would be gained by loss of N_2 and subsequent formation of μ-carbene complexes.

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Registry No. I, 74507-92-9; II, 91759-40-9; III, 91759-41-0; IV, 91759-42-1; V, 91759-44-3; VI, 91759-46-5; VIII, 91759-47-6; N_2CHCO_2Et, 623-73-4.

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