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Coordination and Activation of Diazoalkanes in the Presence of Rh/Ru and Rh/Os Metal Combinations

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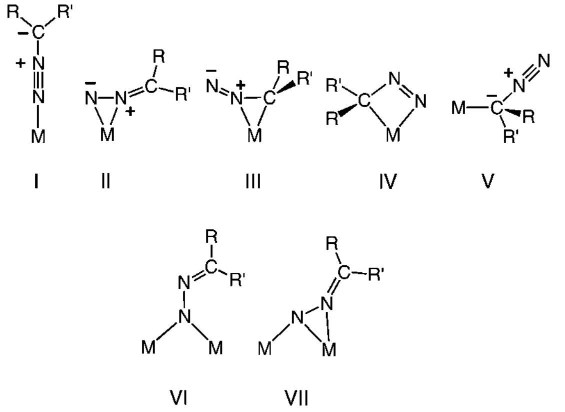
The substituted diazoalkanes—ethyl diazoacetate (EDA), diethyl diazomalonate (DEDM), and trimethylsilyl diazomethane (TMSDM)—react readily with the methylene-bridged tricarbonyl species [RhM(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**5**), Ru (**6**); dppm = μ-Ph$_2$PCH$_2$PPh$_2$) to produce the corresponding substituted olefin (through loss of N$_2$ and subsequent coupling of the diazoalkane-generated alkylidene fragment and the methylene unit), the known tetracarbonyl species [RhM(CO)$_4$(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**1**), Ru (**2**)), and uncharacterized decomposition products. In the reaction of **5** with EDA at −20 °C the intermediate olefin adduct, [RhOs(CO)$_3$(η^2-CH$_2$-CHR)(dppm)$_2$][CF$_3$SO$_3$] (**7**; R = CO$_2$Et) is observed, which decomposes with release of the olefin upon warming. The methylene-bridged tetracarbonyl species [RhM(CO)$_4$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (M = Os(**3**), Ru (**4**)) also react with these diazoalkanes to yield the same products, only at a much slower rate. Attempts to generate the alkylidene-bridged products, analogous to **3** and **4**, by reaction of **1** or **2** with EDA, DEDM, and TMSDM accompanied by loss of N$_2$ instead gave complexes containing the diazoalkane unit. In the reaction with EDA condensation of this unit with a carbonyl ligand occurs accompanied by migration of the diazoalkane hydrogen to the carbonyl oxygen, yielding [RhM(CO)$_3$(μ-η^1:η^1-N$_2$C(COH)CO$_2$Et)(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**8**), Ru (**9**)). The new diazoalkane-like group bridges the metals via the terminal nitrogen, while also binding to the group 8 metal via the enol carbon that originated from a carbonyl group. In the related reaction involving DEDM, substitution of a carbonyl yields [RhM(CO)$_3$(μ-η^1:η^1-N$_2$C(CO$_2$Et)$_2$)(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**10**), Ru (**11**)), in which the intact diazoalkane ligand again bridges via the terminal nitrogen. However, in this case one of the ester carbonyls binds to the group 8 metal, replacing the carbonyl group that was displaced. Although the RhRu compound **2** does not react with TMSDM, the analogous RhOs compound (**1**) does react, yielding [RhOs(CO)$_3$(η^1-N$_2$CHSiMe$_3$)(dppm)$_2$][CF$_3$SO$_3$]] (**12**), in which the TMSDM ligand binds terminally on Os opposite the Rh−Os bond.

Introduction

Diazoalkanes are important reagents in both cyclopropanation reactions[1–5] and for the generation of metallacarbene complexes.[2,5–7] In addition to their role as carbene sources, the coordination chemistry of diazoalkanes is equally rich,[5,6,8,9] displaying a variety of coordination modes, as shown in Chart 1.[6] When bound to a single metal center two coordination modes have commonly been observed, involving either η^1, end-on coordination (type **I**),[10–32] which can assume a number of valence-bond formulations and associated geometries, or the η^2-NN side-on coordination (type **II**).[20,33–39] In addition, three other coordination modes can also be envisioned, although they have yet to be observed: an η^2-NC side-on coordination (type **III**), a four-membered "MCNN" metallacycle (type **IV**), and a η^1-C-bound coordination (type **V**). In binuclear complexes containing two metal centers, diazoalkane coordination at either one of the metals, as illustrated above in structures **I**−**V**, can again occur; however, additional modes are also possible in which the diazoalkane bridges the pair of metals. Two bridging modes have been observed: one in which the diazoalkane ligand bridges both metals through the terminal nitrogen (type **VI**)[40–43] and a related mode in which the diazoalkane again bridges via the terminal nitrogen while also binding in an η^2-fashion to one metal via the pair of nitrogen atoms (type **VII**).[44–54]

Chart 1



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Our primary interest in diazoalkanes has stemmed from their utility as synthons for the generation of alkylidene-bridged bimetallic compounds and in the subsequent carbon−carbon bond formation involving these alkylidene units.[55–65] In a previous study we reported facile methylene-group incorporation and coupling by reaction of $[RhOs(CO)_4(dppm)_2][X]$ (**1**) ($X = CF_3SO_3$; BF_4) with diazomethane to give either $[RhOs(CO)_4(\mu\text{-}CH_2)(dppm)_2][X]$ (**3**), $[RhOs(C_3H_5)(CH_3)(CO)_3(dppm)_2][X]$, or $[RhOs(C_4H_8)(CO)_3(dppm)_2][X]$, depending on reaction temperature.[56,63] On the basis of labeling studies we proposed a reaction sequence in which the coupling of methylene groups occurred via C_2H_4- and C_3H_6-bridged intermediates. Surprisingly, the analogous Rh/Ru species (**2**) did not promote the coupling of methylene groups, but instead incorporated only a single methylene group to give $[RhRu(CO)_4(\mu\text{-}CH_2)(dppm)_2][X]$ (**4**).[58] In order to gain a better understanding of the above methylene-coupling sequence, we set out to generate stable C_2- and C_3-bridged analogues of the putative C_2H_4- and C_3H_6-bridged intermediates noted above. Two strategies were adopted, involving either the reaction of substituted diazoalkanes with the methylene-bridged Rh/Os species **3** and **5**, in attempts to generate substituted C_2 or higher fragments, or through the generation of the alkylidene-bridged products $[RhOs(CO)_n(\mu\text{-}CRR')(dppm)_2][X]$, the chemistry of which, with regard to C−C bond formation, could subsequently be pursued. In addition, we also investigated the related chemistry of the Rh/Ru metal combination, in hopes of learning more about the subtle reactivity differences that can arise from different metal combinations. This chemistry is described herein.

Experimental Section

General Comments. All solvents were dried (using appropriate drying agents), distilled before use, and stored under nitrogen. Reactions were performed under an argon atmosphere using standard Schlenk techniques. Triosmium dodecacarbonyl was purchased from Colonial Metals Inc., while rhodium trichloride hydrate and triruthenium dodecacarbonyl were purchased from Strem Chemicals. Diazomethane was generated from Diazald, $N_2{}^{13}CH_2$ was generated from suitably labeled Diazald, and diazoethane was generated from 1-ethyl-3-nitro-1-nitrosoguanidine (ENNG), all of which were obtained from Aldrich, as were ethyl diazoacetate (EDA) and trimethylsilyl diazomethane (TMSDM; 2 M, Et_2O solution). The compounds $[RhOs(CO)_4(dppm)_2][CF_3SO_3]$ (**1**),[66] $[RhRu(CO)_4(dppm)_2][CF_3SO_3]$ (**2**),[58] $[RhOs(CO)_4(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**3**),[56] $[RhRu(CO)_4(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$

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(**4**),[58] [RhOs(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**5**),[56] and [RhRu(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**6**)[58] were prepared by literature procedures. Diethyl diazomalonate (DEDM) was prepared by a standard route.[67]

The ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.8 and 161.8 MHz, respectively. ^{13}C{^{1}H} NMR and all variable-temperature NMR spectra were recorded on a Varian Unity spectrometer operating at 100.6 MHz for ^{13}C, 161.9 MHz for ^{31}P, and 399.8 MHz for ^{1}H. Infrared spectra were recorded in CH$_2$Cl$_2$ solution on a Nicolet Avatar 370 DTGS spectrometer unless otherwise noted. Elemental analyses were performed by the microanalytical services within the department. Mass spectrometry measurements were performed by the electrospray ionization technique on a Micromass ZabSpec TOF spectrometer in the mass spectrometry facility of the department. Spectroscopic data for all new compounds are given in Table 1. Photolysis experiments were conducted in NMR tubes that were irradiated using a Hanovia 450 W high-pressure mercury lamp placed six inches from the reaction vessel, all of which waSupportings enclosed in a photolysis chamber. Experimental procedures for reactions that gave only unidentified decomposition products appear in the Information.

Preparation of Compounds. (a) [RhOs(CO)$_3$(η^2-CH$_2$=C(H)CO$_2$CH$_2$CH$_3$)(dppm)$_2$][CF$_3$SO$_3$] (7). *Method i:* To a solution of compound **5** (19.2 mg, 0.015 mmol), dissolved in 0.7 mL of CD$_2$Cl$_2$ in an NMR tube, cooled to −78 °C, was added 1.7 μL (0.016 mmol) of N$_2$C(H)CO$_2$Et via a gastight syringe. The NMR tube was then transferred to the NMR probe, which had been precooled to −80 °C, and the reaction monitored by NMR spectroscopy while warming in 10 °C intervals. No change was observed below −20 °C. Holding the sample at −20 °C for 1.7 h resulted in the formation of the product (**7**) in a 3:2 ratio with unreacted compound **5**. After 1.7 h, decomposition of **7** into numerous unidentified products began to occur. *Method ii:* To a stirring deep red solution of compound **5** (30 mg, 0.023 mmol) in 1.5 mL of CH$_2$Cl$_2$ at 20 °C was added 2.4 μL of N$_2$C(H)CO$_2$Et (0.023 mmol). The solution instantly turned light brown and was left to stir for 5 min, then cooled to −80 °C to prevent rapid decomposition of the product. A beige solid was precipitated by the slow addition of 20 mL of pentane (precooled to −80 °C), the solvent was decanted by canula, and the solid was rinsed twice with 5 mL of Et$_2$O and finally dried *in vacuo* (yield 50% as determined by integration of the ^{31}P NMR spectra relative to residual bis(triphenylphosphoranylidene) ammonium chloride; we were unable to separate compound **7** from the numerous unidentified decomposition products). HRMS: *m*/*z* calcd for C$_{60}$H$_{52}$O$_5$P$_4$RhOs (M$^+$ − CF$_3$SO$_3$) 1247.1426, found 1247.1437.

(b) Reaction of Compound 3 with Diazoalkanes at Ambient Temperature. [RhOs(CO)$_4$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**3**) (10 mg, 0.008 mmol) was placed in an NMR tube and dissolved in 0.7 mL of CD$_2$Cl$_2$ at ambient temperature to produce a yellow solution. To this was added 1 equiv of diazoalkane either neat (EDA and DEDM) or as a 2 M ethereal solution (TMSDM). After 60 h the ^{31}P and ^{1}H NMR spectra were recorded. In all cases the products detected were unreacted starting material (ca. 80%), compound **1** (ca. <10%), unidentified decomposition products (ca. 10%), and the corresponding olefin (H$_2$C=CRR′; R = H, R′ = CO$_2$Et, SiMe$_3$; R = R′ = CO$_2$Et).

(c) Reaction of Compound 4 with Diazoalkanes at Ambient Temperature. The reaction of 10 mg of [RhRu(CO)$_4$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**4**) (0.008 mmol) with either EDA, DEDM, or TMSDM was carried out exactly as described in part b. After 60 h ^{31}P and ^{1}H NMR spectroscopy revealed the products to be starting material (ca. 70%), compound **2** (ca. 10%), uncharacterized decomposition products (ca. 20%), and the corresponding olefin, as observed in part b.

(d) Reaction of Compound 5 with Diazoalkanes at Ambient Temperature. One equivalent of either EDA, DEDM, or TMSDM was added to 15 mg (0.011 mmol) of [RhOs(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**5**) in 0.7 mL of CD$_2$Cl$_2$ in an NMR tube at 22 °C. After 1 min the solution became lighter in color, and after 20 min the complete disappearance of **5** and quantitative generation of the substituted olefin accompanied by compound **1** (ca. 10%) and numerous decomposition products (ca. 90%) was confirmed by ^{31}P and ^{1}H NMR spectroscopy.

(e) Reaction of Compound 6 with Diazoalkanes at Ambient Temperature. [RhRu(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**6**) (15 mg, 0.012 mmol) was dissolved in 0.7 mL of CD$_2$Cl$_2$ in an NMR tube at 22 °C. The resulting yellow solution was treated with 1 equiv of each of the above diazoalkanes, causing the solution to lighten in color within seconds. After 20 min ^{31}P and ^{1}H NMR spectroscopy indicated the presence of compound **2** (ca. 10%), the corresponding substituted olefin, and numerous uncharacterized decomposition products (ca. 90%).

(f) Reactions d and e at Low Temperature. Procedures d and e were repeated, but in this instance the solutions were cooled to −78 °C prior to the addition of the diazoalkane. After treatment with the diazoalkane at −78 °C, the sample was inserted into an NMR probe precooled to −80 °C. The reaction was monitored by NMR while warming in 10 °C intervals. In all cases, formation of a short-lived species spectroscopically similar to **7** (ca. 10% by integration) was observed at −20 °C along with numerous unidentified decomposition products. At temperature above −20 °C, only decomposition products were observed.

(g) [RhOs(CO)$_3$(μ-η^1:η^1-N$_2$C(CO$_2$CH$_2$CH$_3$)COH)(dppm)$_2$][CF$_3$SO$_3$] (8). To a yellow solution of **1** (45 mg, 0.034 mmol) in 5 mL of CH$_2$Cl$_2$ at ambient temperature was added 40 μL of ethyl diazoacetate (EDA) as a 1 M ethereal solution. This mixture was allowed to stir for 24 h, during which time no color change was noted. However, the ^{31}P NMR spectrum indicated the complete conversion to the product (**8**). Slow addition of 20 mL of Et$_2$O afforded a yellow powder, which, after decanting the clear supernatant, was rinsed with two 5 mL washings of Et$_2$O before being dried under a stream of argon followed by drying *in vacuo* (yield 88%). HRMS: *m*/*z* calcd for C$_{58}$H$_{50}$O$_6$N$_2$P$_4$RhOs (M$^+$ − CF$_3$SO$_3$) 1289.1280, found 1289.1289.

(h) [RhRu(CO)$_3$(μ-η^1:η^1-N$_2$C(CO$_2$CH$_2$CH$_3$)COH)(dppm)$_2$][CF$_3$SO$_3$] (9). To a stirring yellow solution of 25 mg (0.020 mmol) of **2** in 15 mL of CH$_2$Cl$_2$ at ambient temperature was added 55 μL (0.053 mmol) of N$_2$CH(CO$_2$Et). Over the course of 1 h the yellow solution turned bright orange, at which point it was concentrated to 2 mL followed by the slow addition of Et$_2$O to afford an orange powder. After removal of the clear supernatant, the product was recrystallized from CH$_2$Cl$_2$/Et$_2$O (1 mL/10 mL), yielding bright orange microcrystals, which were isolated by filtration and dried *in vacuo* (yield 75%). Anal. Calcd for C$_{62.1}$H$_{55.2}$Cl$_{0.2}$F$_3$N$_2$O$_{11}$P$_4$RhRuS: C, 52.33; H 3.73; N, 2.07; Cl, 0.52. Found: C, 52.16; H, 3.74; N, 1.98; Cl, 0.54. The presence of 0.1 equiv of CH$_2$Cl$_2$ was confirmed by ^{1}H NMR spectroscopy in THF-*d*$_8$. HRMS: *m*/*z* calcd for C$_{58}$H$_{50}$O$_6$N$_2$P$_4$RhRu (M$^+$ − CF$_3$SO$_3$) 1199.0718, found 1199.0718.

(i) [RhOs(CO)$_3$(μ-η^1:η^1-N$_2$C(CO$_2$CH$_2$CH$_3$)$_2$)(dppm)$_2$][CF$_3$SO$_3$] (10). Compound **1** (53 mg, 0.040 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$ at ambient temperature, yielding a yellow solution. To this solution was added 0.05 mL (0.24 mmol) of N$_2$C(CO$_2$CH$_2$CH$_3$)$_2$, causing the solution to darken slightly. The solution was allowed to stir for 24 h, at which time the solution was dark orange, and only the product, compound **10**, was observed by ^{31}P NMR spectroscopy. The solvent volume was reduced to 2 mL, and a bright yellow powder was precipitated by the addition of 20 mL of Et$_2$O. After removing the clear supernatant, the yellow product was rinsed

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Table 1. Spectroscopic Data for the Compounds

compound	IR (cm^{-1})[a]	NMR[c,d] $\delta(^{31}P\{^1H\})$[c]	NMR[c,d] $\delta(^1H)$[e]	NMR[c,d] $\delta(^{13}C\{^1H\})$[f]
$[RhOs(CO)_3(\eta^2\text{-}CH_2{=}CHCO_2Et)(dppm)_2][CF_3SO_3$ (**7**)	2047 (m), 1981 (m), 1942 (m), 1683 (m),[f] ν(C=C) 1558 (w)	25.3 (dm, 2P, $^1J_{RhP}$ = 113 Hz), −4.1 (dm, 1P, $^2J_{PP}$ = 259 Hz), −10.5 (dm, 1P, $^2J_{PP}$ = 259 Hz)	dppm: CH_2: 4.47 (br, m, 1H), 4.27 (br, m, 1H), 4.10 (br, m, 1H), 3.12 (br, m, 1H) CH_2CHCO_2Et: CH_2: 1.08 (br, m, 1H, $^3J_{HH}$ = 8 Hz, $^1J_{HC}$ = 144 Hz), 1.72 (br, m, 1H, $^3J_{HH}$ = 8 Hz, $^1J_{HC}$ = 157 Hz); CH: 2.77 (br, m, 1H, br, s, 1H, $^3J_{HH}$ = 8 Hz); CH_2: 4.23 (qq, 2H, $^3J_{HH}$ = 7 Hz); CH_3: 1.32 (t, 3H, $^3J_{HH}$ = 7 Hz)	CH_2CHCO_2Et: CH_2: 3.80 (s) OsCO: 182.8 (t, $^2J_{CP}$ = 8.0 Hz), 185.5 (t, $^2J_{CP}$= 7.1 Hz); RhCO: 182.5 (dt, $^1J_{RhC}$ = 77.6, $^2J_{CP}$ = 16.8)
$[RhOs(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2C(CO_2CH_2CH_3)COH)(dppm)_2][CF_3SO_3]$ (**8**)[b]	3058 (m), 2020 (s), 1970 (s, br), 1633 (s),[f] 1466 (m)[g]	0.3 (m, 2P), 28.1 (dm, 2P, $^1J_{RhP}$ = 147 Hz)	dppm: CH_2: 3.22 (m, 2H), 2.74 (m 2H) CO_2Et: CH_2: 4.42 (q, 2H, $^3J_{HH}$ = 7 Hz); CH_3: 1.51 (t, 3H, $^3J_{HH}$ = 7 Hz) COH: 11.04 (s, 1H)	OsCO: 177.9 (t, $^2J_{CP}$ = 8.5 Hz), 179.6 (t, $^2J_{CP}$ = 13.9 Hz); RhCO: 195.5 (dt, $^1J_{RhC}$ = 63.2 Hz, $^2J_{CP}$ = 15.6 Hz) dppm: CH_2: 17.9 (m) CO_2Et: CH_2: 61.2 (s); CH_3: 14.7 (s) COH: 231.6 (t, $^2J_{CP}$ = 8.3 Hz)
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2C(CO_2CH_2CH_3)COH)(dppm)_2][CF_3SO_3]$ (**9**)	3054 (s), 2026 (m), 1969 (m), 1997 (m), 1691 (m), [f] 1550 (w)[g]	37.0 (m, 2P), 28.2 (dm, 2P, $^1J_{RhP}$ = 148 Hz)	dppm: CH_2: 3.26 (m, 2H), 2.69 (m, 2H) CO_2Et: CH_2: 4.38 (q, 2H, $^3J_{HH}$ = 7 Hz), CH_3: 1.50 (t, 3H, $^3J_{HH}$ = 7 Hz) COH: 11.01 (s)	RuCO: 194.3 (t, $^2J_{CP}$ = xx Hz), 197.8 (t, $^2J_{CP}$ = 10.7 Hz); RhCO: 196.8 (dt, $^1J_{RhC}$ = 64.7 Hz, $^2J_{CP}$ = 15 Hz) COH: 244.1 (t, $^2J_{CP}$ =)
$[RhOs(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2C(CO_2Et)_2)(dppm)_2][CF_3SO_3]$ (**10**)	2027 (m), 1992 (s), 1963 (m), 1699 (m)[f], 1690 (m),[f] 1510 (s)[g]	11.1 (m, 2P), 26.4 (dm, 2P, $^1J_{RhP}$ = 151 Hz)	dppm: CH_2: 3.16 (m, 2H), 3.13 (m, 2H) CO_2Et: CH_2: 4.37 (q, 2H, $^3J_{HH}$ = 7 Hz), 1.86 (q, 2H, $^3J_{HH}$ = 7 Hz); CH_3: 1.41 (t, 3H, $^3J_{HH}$ = 7 Hz), 0.62, 3H, $^2J_{HH}$ = 7 Hz)	OsCO: 172.0 (t, $^2J_{CP}$ = 7.6 Hz), 180.0 (t, $^2J_{PC}$ = 6.0 Hz); RhCO: 195.5 (dt, $^1J_{RhC}$ = 63.2 Hz, $^2J_{CP}$ = 15.6 Hz) dppm: CH_2 20.3 (m) CO_2Et: CH_3: 13.3 (s), 15.2 (s); CH_2: 60.0(s), 61.2 (s) N_2C: 125.9 (br, s); CO: 165.8 (s), 153.0
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2C(CO_2Et)_2)(dppm)_2][CF_3SO_3]$ (**11**)	2036 (m), 1996 (s), 1969 (m), 1725 (w),[f] 1641 (m),[f] 1484 (m)[g]	37 (m, 2P), 28.3 (dm, 2P, $^1J_{RhP}$ = 148 Hz)	dppm: CH_2 3.24 (m, 2H), 3.08 (m, 2H) CO_2Et: CH_2: 4.35 (q, 2H, $^3J_{HH}$ = 7 Hz), 1.91 (q, 2H, $^3J_{HH}$ = 7 Hz); CH_3: 1.40 (t, 3H, $^3J_{HH}$ = 7 Hz), 0.62 (t, 3H, $^3J_{HH}$ = 7 Hz)	RuCO: 197.0 (bs), 195.6 (bs); RhCO: 195.4 (bd, $^1J_{RhP}$ = 63.7 Hz dppm: CH_2: 13.5 (m) CO_2Et: CH_2 61.0(s), 59.8 (s); CH_3: 15.4 (s), 13.5 (s); C(O)O: 165.7 (s), 155.3 (s)
$[RhOs(CO)_3(\eta^1\text{-}N_2CH(Si(CH_3)_3))(dppm)_2][CF_3SO_3]$ (**12**)	2059 (s), 1977 (m), 1804 (m)	1.0(m, 2P), 26.0 (dm, 2P, $^1J_{RhP}$ = 115 Hz)	dppm: CH_2: 4.03 (m, 4H) $N_2CH(Si(CH_3)_3)$: CH: 2.32 (s, 1H), CH_3: 0.41 (s)	RhCO: 181.2 (dm, 1C, $^1J_{RhC}$ = 80.3 Hz) OsCO: 194.6 (m, 2C, $^1J_{RhC}$ = 3.3 Hz)
$RhOs(CO)_2(PMe_3)(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2C(CO_2CH_2CH_3)_2(dppm)_2][CF_3SO_3]$ (**13**)	2092 (m), 2003 (m), 1752 (m), 1686 (m, br)[f]	−18.5(dt, 1P, $^1J_{RhP}$ = 129 Hz, $^2J_{PP}$ = 42 Hz), 12.1 (m, 2P), 28.4 (dm, 2P, $^1J_{RhP}$ = 162 Hz)	dppm: CH_2 3.08 (m, 2H), 2.87 (m, 2H) CO_2Et: CH_2 4.28 (q, 2H, $^3J_{HH}$ = 7 Hz), 3.44 (q, 2H, $^3J_{HH}$ = 7 Hz); CH_3 1.38 (t, 3H, $^3J_{HH}$ = 7 Hz), 1.16 (t, 3H, $^3J_{HH}$ = 7 Hz) $P(CH_3)_3$: CH_3 0.47 (d, 9H, $^2J_{HP}$ = 8 Hz)	OsCO: 171.0 (t, $^2J_{CP}$ = 8 Hz), 181.0 (t, $^2J_{CP}$ = 6.5 Hz)

[a] IR abbreviations: s = strong, m = medium, br = broad. Dichloromethane solution; in units of cm^{-1}. [b] IR obtained by IR microspcope. [c] NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, bs = broad singlet, bd = broad doublet. NMR data at 27 °C in CD_2Cl_2 unless otherwise indicated. [d] ^{31}P chemical shifts referenced to external 85% H_3PO_4. [e] ^1H and ^{13}C chemical shifts referenced to TMS. Chemical shifts for the phenyl carbons not given. [f] ν(CO) for CO_2Et fragment. [g] ν(C=N).

twice with 5 mL of Et_2O and the product dried under an argon stream and then *in vacuo* (yield 85%). Anal. Calcd for $C_{61.1}H_{54.2}N_2O_{10}F_3SP_4Cl_{0.2}RhOs$: C, 49.19; H, 3.66; N 1.89. Found: C, 48.70; H, 4.02; N, 1.73. The presence of 0.1 equiv of $CH_2Cl_2$was confirmed by ^1H NMR spectroscopy in THF-d_8. HRMS: *m*/*z* calcd for $C_{60}H_{54}O_7N_2P_4RhOs$ ($M^+ - CF_3SO_3$) 1333.1542, found 1333.1526.

(j) [RhRu(CO)$_3$(μ-η^1:η^1-$N_2C(CO_2CH_2CH_3)_2$)(dppm)$_2$][CF_3SO_3] (11). A 36 mg (0.028 mmol) amount of **2** was dissolved in 20 mL of CH_2Cl_2 at ambient temperature, and 24 μL of $N_2C(CO_2Et)_2$(0.14 mmol) was added. The resulting yellow solution darkened slightly within 15 min. After 2 h, only compound **11** remained, as confirmed by ^{31}P NMR spectroscopy of the deep red solution, from which a salmon-red product was precipitated by the slow addition of 30 mL of Et_2O. After removing the solvent, the precipitate was rinsed with two 5 mL portions of Et_2O and dried under a stream of argon then *in vacuo* (yield 82%). Anal. Calcd for $C_{61}H_{54}F_3N_2O_{10}SP_4RhRu$: C, 52.63; H, 3.91; N, 2.01. Found: C, 52,26; H, 3.93; N, 1.91. HRMS: *m*/*z* calcd for $C_{60}H_{54}O_7N_2P_4RhRu$ ($M^+ - CF_3SO_3$) 1243.0980, found 1243.0980.

(k) [RhOs(CO)$_3$(η^1-$N_2C(H)Si(CH_3)_3$)(dppm)$_2$][CF_3SO_3] (12). *Method i*: A yellow solution of compound **1** (55 mg, 0.042 mmol) in 5 mL of CH_2Cl_2 at ambient temperature was treated with 0.30 mL of a 2 M solution of $N_2C(H)Si(CH_3)_3$ in Et_2O. After 16 h $^{31}P\{^1H\}$ NMR spectroscopy revealed 25% conversion to compound **12**, and after 4 days $^{31}P\{^1H\}$ NMR spectroscopy showed compound **12** as the only detectable compound; however ^1H-NMR spectroscopy revealed numerous decomposition products. The solvent was removed *in vacuo* and the crude brown residue recrystallized from CH_2Cl_2/Et_2O to afford oily brown microcrystals of the product which decomposed in the solid within hours. The solid was rinsed several times with Et_2O before being dried *in vacuo* (yield 72%). *Method ii*: If the same procedure noted in the first method was repeated, except a slow stream of Ar was also passed over the solution, the reaction proceeded to completion in 16 h. Anal. Calcd for $C_{58}H_{54}N_2F_3O_6P_4SSiRhOs$: C, 49.43; H, 3.86; N, 1.99; S, 2.28. Found: C, 49.59; H, 4.03; N, 1.23; S, 2.42. MS: *m*/*z* = 1147. The elemental analysis was performed within 1 h of isolation of the solid sample to minimize decomposition.

(l) [RhOs(CO)$_2$(PMe_3)(μ-η^1:η^1-$N_2C(CO_2CH_2CH_3)_2$)(dppm)$_2$]-[CF_3SO_3] (13). In an NMR tube at ambient temperature, 10 mg of compound **10** (0.0068 mmol) was dissolved in 0.7 mL of CD_2Cl_2, to which was added 7 μL of a 1 M solution of PMe_3 (in toluene) (0.007 mmol). After 2.5 days quantitative conversion to the product (**13**) was confirmed by ^{31}P NMR spectroscopy. The solution was left to stand for a period of 2 weeks, over which time no further transformations were observed by ^{31}P NMR spectroscopy. Anal. Calcd for $C_{63}H_{63}F_3N_2O_{10}P_5RhOsS$: C, 48.97; H 4.11; N, 1.81; S, 2.08. Found: C, 49.18; H, 4.53; N, 1.74; S, 2.97.

(m) Photolysis Experiments. Compounds **8**, **9**, **10**, and **11** (ca. 15 mg) were each dissolved in 0.7 mL of CD_2Cl_2 in separate NMR tubes. The samples were irradiated in the photolysis chamber described above for 16 h and monitored by ^{31}P NMR spectroscopy. No changes were observed.

(n) Thermolysis Experiments. *Method i*: Compounds **8**, **9**, **10**, and **11** (ca. 25 mg) were each dissolved in 2 mL of freshly distilled THF. The solutions were left to reflux and the reactions observed by $^{31}P\{^1H\}$ NMR spectroscopy. No new species were noted after 16 h. *Method ii*: The reaction described in method i was repeated using freshly distilled toluene instead of THF. Again, no new species were observed.

X-ray Data Collection. Yellow-orange crystals of [RhOs(CO)$_3$(μ-η^1,η^1-N=NC(COH)CO_2Et)(dppm)$_2$][CF_3SO_3](**8**)·$C_2H_4Cl_2$ were obtained by slow evaporation of a 1,2-dichloroethane solution of the compound. Data were collected at −80 °C on a Bruker PLATFORM/SMART 1000 CCD diffractometer[68] using Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 5554 reflections from the data collection. The space group was determined to be $P\bar{1}$(No. 2). The data were corrected for absorption through use of Gaussian integration (involving face-indexing of the crystal). See Table 2 for a summary of crystal data and X-ray data collection information.

Structure Solution and Refinement. The structure of **8** was solved using the Patterson location of heavy atoms and structure expansion routines as implemented in the DIRDIF-96[69] program system. Refinement was completed using the program SHELXL-97. Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons, with the exception of hydrogen H(40), which was located and freely refined. The final model for **6** was refined to values of $R_1(F) = 0.0281$ (for 11 411 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0765$ (for all 12 323 independent data).

Results and Compound Characterization

(a) Treatment of Methylene-Bridged Complexes with Diazoalkanes. Reaction of the methylene-bridged tetracarbonyl species [RhM(CO)$_4$(μ-CH_2)(dppm)$_2$][CF_3SO_3] (M = Os (**3**), Ru (**4**)) with either ethyl diazoacetate (EDA), trimethylsilyldiazomethane (TMSDM), or diethyldiazomalonate (DEDM) results in the generation of the respective free olefins over the period of several days, as verified by comparison of their NMR spectra to those reported in the literature ($H_2C{=}CRR'$; R = H, R′ = CO_2Et, $SiMe_3$; R = R′ = CO_2Et).[70] The formation of these olefins corresponds to expected coupling of the diazoalkane-generated alkylidene unit and the methylene group. In all cases, the phosphorus-containing compounds remaining were identified by $^{31}P\{^1H\}$ NMR spectroscopy as unreacted compound **3** or **4**, the respective byproduct **1** or **2**, and numerous uncharacterized decomposition products all in varying proportions depending on the diazoalkane. In contrast, the tricarbonyl analogues [RhM(CO)$_3$(μ-CH_2)(dppm)$_2$][CF_3SO_3] (M = Os (**5**), Ru (**6**)) react instantly with these diazoalkanes at ambient temperature, resulting in the rapid evolution of the free olefin, together with the respective compound **1** or **2**, again accompanied by numerous uncharacterized decomposition products as determined by ^{31}P NMR spectroscopy. This reactivity is summarized in Scheme 1. We assume that formation of the tetracarbonyl species **1** and **2**, from the tricarbonyl precursors **5** and **6**, respectively, results from carbonyl scavenging from the decomposition products.

Quenching the reaction involving compound **5** and EDA by cooling the sample to −20 °C allows the isolation of a new species, [RhOs(η^2-$H_2C{=}CHCO_2Et$)(CO)$_3$(dppm)$_2$][CF_3SO_3] (**7**), as also shown in Scheme 1. In the $^{31}P\{^1H\}$ NMR spectrum, compound **7** gives rise to three complex multiplets at δ 25.3, −4.1, and −10.5 in a 2:1:1 intensity ratio. The two high-field signals appear as the C and D portion of an ABCDX spin system (X = ^{103}Rh) and clearly correspond to the inequivalent phosphorus nuclei at the Os-bound ends of the dppm ligands, on the basis of the higher-field chemical shifts[66] and the absence of Rh coupling. The low-field resonance of double intensity corresponds to the two accidentally degenerate A and B resonances for the Rh-bound ends of the dppm ligand and appears as an approximate doublet of multiplets with strong

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(68) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

(69) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-96 program system*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1996.

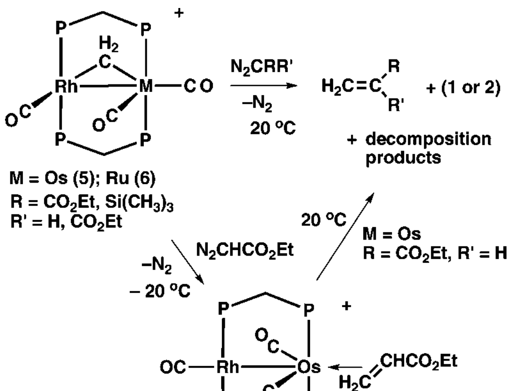
(70) http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi.

Table 2. Crystallographic Experimental Details for Compound 8

A. Crystal Data	
formula	$C_{61}H_{54}Cl_2F_3N_2O_9OsP_4RhS$
fw	1536.01
cryst dimens (mm)	0.63 × 0.37 × 0.28
cryst syst	triclinic
space group	$P\bar{1}$(No. 2)
unit cell params[a]	
a (Å)	11.3899(7)
b (Å)	15.0631(9)
c (Å)	18.4369(11)
α (deg)	87.7008 (12)
β (deg)	76.4194(11)
γ (deg)	88.4252(11)
V (Å^3)	3071.7(3)
Z	2
ρ_{calcd} (g cm^{-3})	1.661
μ (mm^{-1})	2.627
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[68]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	−80
scan type	ω scans (0.2°) (20 s exposures)
data collection 2θ limit (deg)	52.76
total no. of data collected	17 696 ($-14 \leq h \leq 14$, $-17 \leq k \leq 18$, $-23 \leq l \leq 23$)
no. of indep reflns	12 323 ($R_{int} = 0.0162$)
no. of observed reflns	11 411 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (DIRDIF-99[69])
refinement method	full-matrix least-squares on F^2 (SHELXL-97[b])
absorp corr method	Gaussian integration (face-indexed)
range of transmn factors	0.5205−0.2696
no. of data/restraints/params	12 323 [$F_o^2 \geq -3\sigma(F_o^2)$]/0/761
goodness-of-fit (S)[c]	1.038 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[d]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0281
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0765
largest diff peak and hole (e Å^{-3})	1.749 and −1.048

[a] Obtained from least-squares refinement of 5554 centered reflections. [b] Sheldrick, G. M. *SHELXL-97*, Program for crystal structure determination; University of Göttingen: Germany, 1997. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0454P)^2 + 3.7359P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$). [d] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Scheme 1



coupling to Rh (approximately 113 Hz). The strong coupling between the pair of signals corresponding to the ^{31}P nuclei bound to Os ($^2J_{PcPd}$ = 259 Hz) indicates a mutually *trans* phosphine arrangement at this metal. In the ^{13}C{^{1}H} NMR spectrum of **7** three carbonyl resonances appear: two triplets at δ 182.8 and 185.5, displaying no Rh coupling, correspond to two terminally bound carbonyls on Os, and a doublet of triplets at δ 182.5, showing strong Rh coupling ($^1J_{RhC}$ = 77.6 Hz), corresponds to the carbonyl that is terminally bound to Rh. If $^{13}CH_2$-enriched compound **5** is used in the above reaction, an additional ^{13}C{^{1}H} resonance at δ 3.80 in the ^{13}C{^{1}H} NMR spectrum, corresponding to the CH_2 end of the coordinated olefin, is observed that shows no coupling to any of the ^{31}P nuclei or to Rh. The ^{1}H NMR spectrum of **7** shows two resonances at δ 1.08 and 1.72, both of which display coupling of approximately 8 Hz to an additional proton resonance at δ 2.77. These three protons correspond to the three olefinic protons of the coordinated olefin. Although one might expect different *cis*/*trans* coupling constants for the olefinic protons, rehybridization of the olefin upon coordination presumably results in equivalent coupling involving the pseudo*cis* and pseudo*trans* protons. In the $^{13}CH_2$-enriched sample of compound **7** the two high-field protons display coupling to the ^{13}C nucleus of 144 and 157 Hz coupling, respectively, indicating that they correspond to this CH_2 group. These one-bond C−H coupling constants lie between those typical for an olefin (ca. 160 Hz) and that of an alkane (ca. 130 Hz),[71] reflecting some degree of rehybridization, as noted above. The dppm methylene protons appear as four separate broad multiplets at δ 4.47, 4.27, 4.10, and 3.12, indicating a lack of front−back and top−bottom symmetry, rendering each proton chemically unique. This suggests that olefin rotation is slow on the NMR time scale. Finally, the ethyl fragment of the ethyl acrylate ligand resonates at δ 1.32 (CH_3) and 4.23 (CH_2), similar to that of free ethyl acrylate.[70] We have ruled out an olefin-bridged structure for compound **7** since in such an arrangement the olefin could be considered a 1,2-dimetalated ethane unit, with essentially complete rehybridization of the olefinic carbons to sp^3. This is

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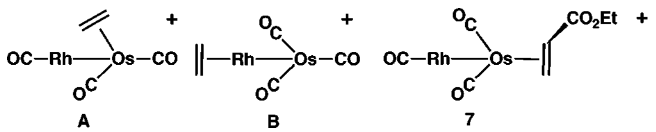
(71) Silverstein, R. M.; Webster, F. X. *Spectroscopic Identification of Organic Compounds*; John Wiley and Sons, Inc.: New York, 1998.

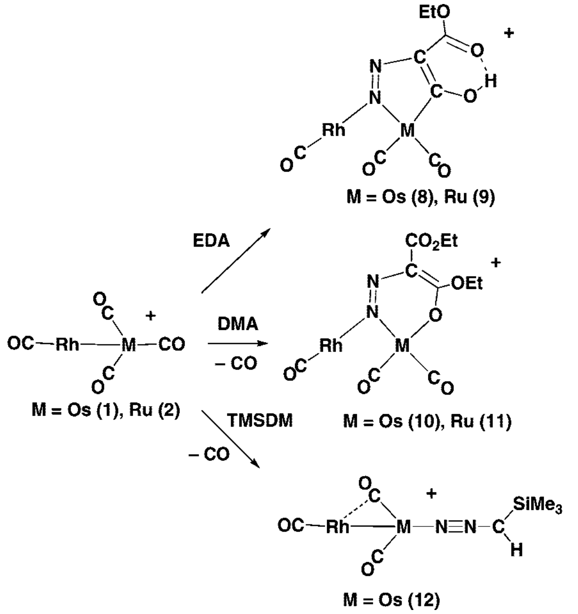
Chart 2



inconsistent with the large C−H coupling constants noted above. In addition, the absence of spin−spin coupling involving either end of the olefin and the Rh nucleus establishes that the ethyl acrylate ligand is bound solely to Os. Compound **7** can be compared to two related monoethylene adducts, [RhOs(C$_2$H$_4$)(CO)$_3$(dppm)$_2$][BF$_4$] (**A**) and [RhOs(CO)$_3$(C$_2$H$_4$)(dppm)$_2$][BF$_4$] (**B**), shown in Chart 2[56b] (dppm ligands omitted). A structure like **B** can be immediately ruled out, since as established above, the olefin is bound to Os while one carbonyl is on Rh. In addition, the spectral data do not fit structure **A**. It has been established that terminal carbonyls that lie adjacent to another metal, and therefore having weak interactions with it, usually resonate downfield of those that lie remote from the adjacent metal;[72] this is clearly seen in compound **A**, in which the chemical shifts of the two Os-bound carbonyls differ by 10 ppm. In contrast, the pair of Os-bound carbonyls in **7** are very similar, having a chemical shift difference of only 2.7 ppm. Furthermore, the relatively low-field shift for the Os-bound carbonyls suggests that they are adjacent to the Rh center, possibly interacting weakly with this second metal (generally, terminal carbonyls on third-row metals appear significantly upfield from those of the second-row analogues). On the basis of the above NMR data, the structure shown in Scheme 1 and Chart 2 is proposed in which an ethyl acrylate ligand is bound to Os in an η^2 fashion opposite the metal−metal bond with both Os-bound carbonyls adjacent to the metal−metal bond. The IR spectrum of **7** shows a stretch for the CO$_2$Et group at 1683 cm^{-1} and three terminally bound carbonyl ligands (2047, 1981, and 1942 cm^{-1}). In addition, a weak band at 1558 cm^{-1} can be assigned to the olefinic C−C stretch shifted significantly from that of free ethyl acrylate (1638 cm^{-1}).[70]

Compound **7** is labile, decomposing in solution above −20 °C into free ethyl acrylate, compound **1**, and numerous unidentified phosphorus-containing products. Attempts to displace the ethyl acrylate ligand in **7** by ethylene, under an ethylene atmosphere, gave no evidence of an ethylene adduct over the temperature range from 22 to −80 °C. Again, only decomposition of **7** resulted over time or upon warming. Although we have not been able to isolate analogous olefin adducts in the reactions of **5** with the other substituted diazoalkanes, we have observed such species in small quantities (<10% by integration of all phosphorus-containing species) in the ^{31}P{^{1}H} NMR spectra at −20 °C, having very similar spectra to those of **7**. We assume that the greater lability of these intermediates results from destabilizing repulsions involving the additional ester substituent in the case of the DEDM reaction or the larger trimethylsilyl substituent in the case of TMSDM. In the case of the Rh/Ru complex **6**, no olefin adduct analogous to **7** was observed in any of the diazoalkane reactions, although the same olefins were ultimately obtained.

Scheme 2



(b) Diazoalkane Complexes. In attempts to generate alkylidene-bridged complexes analogous to compounds **3** and **4** via N$_2$ loss from the parent diazoalkane, the reactions of **1** and **2** with a number of substituted diazoalkanes were attempted. Treatment of both compounds **1** and **2** with EDA yields the unusual products [RhM(CO)$_3$(μ-η^1:η^1-$\underline{\mathrm{N}}$=NC(CO$_2$Et)$\underline{\mathrm{C}}$OH)(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**8**), Ru (**9**)), diagrammed in Scheme 2 (dppm ligands omitted). High-resolution mass spectrometry for both products verifies that dinitrogen loss has not occurred from the diazoalkane molecule, and this is confirmed by the X-ray structure of **8** shown in Figure 1. The X-ray study also demonstrates that although N$_2$ loss has not occurred, the diazoalkane molecule has transformed into a new diazoalkane-like moiety via condensation with a carbonyl ligand, accompanied by hydrogen migration from the diazoalkane carbon to the carbonyl oxygen to give and metalla-enol functionality. Migratory insertions, involving carbonyl ligands,

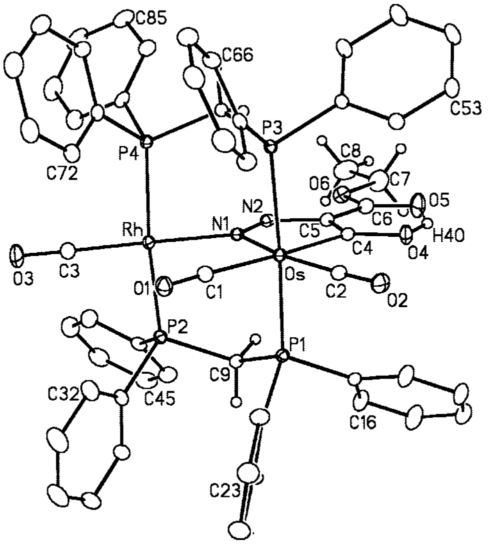


Figure 1. Perspective view of the [RhOs(CO)$_3${μ:η^1,η^1-$\underline{\mathrm{N}}$=NC($\underline{\mathrm{C}}$OH)CO$_2$Et}(dppm)$_2$]$^+$ complex cation of compound **8**, showing the atom-labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl hydrogens, which are not shown.

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[72] George, D. S. A.; McDonald, R.; Cowie, M. *Organometallics* **1998**, *17*, 2553.

Table 3. Selected Distances and Angles for Compound 8

Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Os	Rh	3.3206(3)	O(4)	H(40)	0.87(6)
Os	N(1)	2.088(2)	O(5)	C(6)	1.227(5)
Os	C(1)	1.976(3)	O(5)	H(40)	1.85(6)[a]
Os	C(2)	1.904(3)	O(6)	C(6)	1.326(4)
Os	C(4)	2.055(3)	O(6)	C(7)	1.464(5)
Rh	N(1)	2.023(3)	N(1)	N(2)	1.270(4)
Rh	C(3)	1.842(4)	N(2)	C(5)	1.402(4)
O(1)	C(1)	1.139(4)	C(4)	C(5)	1.391(4)
O(2)	C(2)	1.145(4)	C(5)	C(6)	1.455(5)
O(3)	C(3)	1.143(5)	C(7)	C(8)	1.473(7)
O(4)	C(4)	1.328(4)			

Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
N(1)	Os	C(1)	98.9(1)	Os	C(1)	O(1)	173.3(3)
N(1)	Os	C(2)	166.8(1)	Os	C(2)	O(2)	174.3(3)
N(1)	Os	C(4)	75.6(1)	Rh	C(3)	O(3)	178.9(4)
C(1)	Os	C(2)	94.2(1)	Os	C(4)	O(4)	125.0(2)
C(1)	Os	C(4)	174.5(1)	Os	C(4)	C(5)	114.1(2)
C(2)	Os	C(4)	91.3(1)	O(4)	C(4)	C(5)	120.9(3)
N(1)	Rh	C(3)	176.5(1)	N(2)	C(5)	C(4)	117.1(3)
C(4)	O(4)	H(4O)	114(4)	N(2)	C(5)	C(6)	121.3(3)
C(6)	O(6)	C(7)	115.9(3)	C(4)	C(5)	C(6)	121.6(3)
Os	N(1)	Rh	107.8(1)	O(5)	C(6)	O(6)	122.3(3)
Os	N(1)	N(2)	119.9(2)	O(5)	C(6)	C(5)	121.8(3)
Rh	N(1)	N(2)	132.3(2)	O(6)	C(6)	C(5)	115.9(3)
N(1)	N(2)	C(5)	113.3(3)	O(6)	C(7)	C(8)	108.0(2)

[a] Nonbonded distance.

are very common[73] and have been observed with diazoalkane-generated[74] or metal-bound[75] alkylidene groups, and with nitrido groups that have resulted from N−N bond cleavage in diazoalkanes.[76] However, we are unaware of any report involving condensation of a carbonyl ligand with an intact diazoalkane group within a metal complex. The new diazo-containing group in **8** binds in a bridging arrangement bound to both metals through the terminal nitrogen (not unlike structure **VI** shown in Chart 1) while chelating to Os via the enol carbon to give a five-membered Os−N−N−C−C metallacycle. Within this metallacycle, the bond lengths and angles, given in Table 3, are consistent with the valence-bond formulation shown in Scheme 2. Therefore, the N(1)−N(2) distance (1.270(4) Å) is that of a typical N═N double bond, while the N(2)−C(5) distance (1.402(4) Å) is as expected for a single bond between sp^2-hybridized N and C atoms.[77] The newly formed C(4)−C(5) bond (1.391(4) Å) is typical of an enolic double bond,[77] while the C(5)−C(6) and C(4)−O(4) distances (1.455(5), 1.328(4) Å, respectively) are consistent with single bonds within such groups. Within the N$_2$-containing metallacycle, the angles are all somewhat smaller (range 113.3(3)−119.9(2)°) than the idealized value for sp^2 hybridization, reflecting a degree of strain within this group, as a result of the acute N(1)−Os−C(4) bite angle (75.6(1)°). The diazo-containing fragment bridges in a close-to-symmetrical manner in which the Os−N(1) distance is only slightly longer than Rh−N(1) (2.088(2) vs 2.023(3) Å).

The X-ray study has also allowed the unambiguous location and successful refinement of the enol hydrogen, placing it within obvious bonding distance of the enol oxygen (O(4)−H(40) = 0.87(6) Å), but also in a position to be hydrogen-bonded to the carbonyl oxygen of the CO$_2$Et group (O(5)−H(40) = 1.85(6) Å), with this separation being significantly less than the sum of the van der Waals radii of 2.6 Å. The presence of hydrogen bonding is further substantiated by the planar arrangement of the six-membered ring that results (see Figure 1), involving the enol and carbonyl functionalities; a repulsive interaction between H(40) and O(5) would lead to rotation of the OH group out of the enol plane.

The diazo-containing ligand in compounds **8** and **9** functions as a dianionic 6 e$^-$ donor to the Rh(I)/M(II) (M = Os, Ru) centers. In keeping with these oxidation-state formulations, the coordination geometry at Rh is square planar, while that of Os is octahedral. This formulation differs from that shown in the compounds displaying structure **VI** (Chart 1) owing to the additional enolate functionality, which donates an additional pair of electrons.

The transformation of compounds **1** and **2** into the products **8** and **9**, respectively, is irreversible; addition of CO to either of the products gives no further reaction and does not regenerate **1** or **2**, most likely a result of the condensation and hydrogen migration steps, which in this case appear irreversible. For compounds **8** and **9** the spectral parameters are closely comparable (see Table 1), so compound **9** is assumed to have the same structure as that established for **8**. In the ^{1}H NMR spectrum of **8** the dppm methylene and the ethyl group resonances are as expected, while the hydroxyl proton appears as a singlet at δ 11.04, as is characteristic of a hydrogen-bonded hydroxyl proton.[71] ^{13}C{^{1}H} NMR data show only three terminal carbonyl resonances; two triplets at δ 177.9 and 179.6 correspond to the Os-bound groups, while a doublet of triplets at δ 195.5, with 63.2 Hz coupling to the Rh nucleus, corresponds to the Rh-bound CO (surprisingly, in this case the Os-bound carbonyl that is adjacent to Rh cannot be differentiated from the one that occupies the remote position). The enol carbon is observed as a triplet at δ 231.6 ($^2J_{CP}$ = 8.3 Hz) with coupling to the pair of Os-bound ^{31}P nuclei. A solution IR of a sample of **8** shows two terminal carbonyl stretches (2020 cm^{-1} (s), 1970 cm^{-1} (s, br)), a stretch at 1633 cm^{-1}, attributed to the CO$_2$Et group, and a stretch at 3058 cm^{-1}, which is assigned to the OH functionality.

The corresponding reactions of compounds **1** and **2** with DEDM yield the respective diazoalkane-bridged complexes [RhM(CO)$_3$(μ-η^1:η^1-N═NC(CO$_2$Et)$_2$)(dppm)$_2$][CF$_3$SO$_3$] (M = Os (**10**), Ru (**11**)) (Scheme 2), in which the DEDM ligand is again proposed to bridge via the terminal nitrogen. Although binding of DEDM is accompanied by the loss of one carbonyl, the reactions cannot be reversed by addition of CO. The presence of an N$_2$ moiety within these complexes is verified by HRMS and elemental analysis, while the loss of a carbonyl is seen in the ^{13}C{^{1}H} NMR spectra of ^{13}CO-enriched samples, in which only three equal intensity resonances are observed. For compound **11**, the pair of Ru-bound carbonyls appear at δ 197.0 and 195.6, whereas the one bound to Rh appears at δ 195.4, with typical coupling (63.7 Hz) to Rh. All resonances display typical patterns consistent with coupling to the adjacent pair of ^{31}P nuclei. The ester carbonyls on the DEDM ligand appear at δ 165.7 and 155.3, demonstrating the inequivalence of these two ester groups. This inequivalence is also evident in the ethyl group resonances in the ^{1}H NMR spectrum with one group appearing at δ 1.91 (CH$_2$) and 0.62 (CH$_3$) while the other appears at δ 4.35 (CH$_2$) and 1.40 (CH$_3$). The NMR spectral parameters for the Os analogue very much mirror those given

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(73) (a) Collman, J. P.; Hegedus, L. S.;. Norton, J. S.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 12. (b) Niu, S.; Hall, M. B. *Chem. Rev* **2000**, *100*, 353.

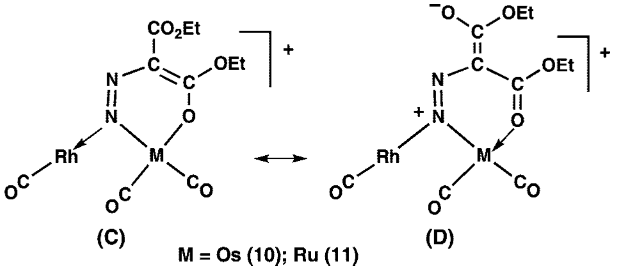
(74) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133.

(75) Proulx, G.; Bergman, R. G. *Science* **1993**, *259*, 661.

(76) Li, B.; Tan, X.; Xu, S.; Song, H.; Wang, B. *J. Organomet. Chem.* **2008**, *693*, 667.

(77) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

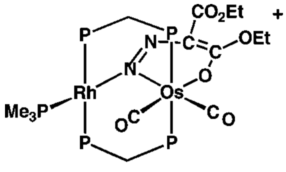
Chart 3



above, except that the Os-bound carbonyls appear upfield to those bound to Ru, as is typically the case.

On the basis of the significant inequivalence of the pair of ester groups in each complex and the presence of only two Ru- or Os-bound carbonyls, as was observed in compounds **8** and **9**, we propose that coordination of one of the ester groups to Ru or Os occurs, as diagrammed for one valence-bond representation in Scheme 2. Similar binding of DEDM, via both nitrogen and an ester carbonyl, has been proposed.[36] The valence-bond representation shown in Scheme 2 for compounds **10** and **11** would be expected to give rise to two very different ester carbonyl stretches in the IR spectrum: one at a value close to that of free DEDM and another (corresponding to the coordinated ester) at a significanty lower frequency. In the case of the Ru species (**11**) these stretches are observed at 1725 and 1641 cm^{-1}, in support of the formulation given. This lowering of the ester carbonyl stretches has also been observed by Eisenberg et al.[78] However, for the Os analogue (**10**) the ester stretches both appear at the intermediate values, 1699 and 1690 cm^{-1}, suggesting a structure in which there is significant delocalization over the pair of ester groups. Two limiting valence-bond formulations for the coordinated DEDM ligand in compounds **10** and **11** are shown in Chart 3 (dppm groups omitted). Structure **C** corresponds to the bonding extreme proposed in the Rh/Ru species (**11**), while the structure proposed for the Rh/Os species (**10**) is presumably a hybrid of **C** and **D**. In either case, the ligand functions as a dianionic 6 e$^-$ donor to the Rh(I)/M(II) centers (M = Os, Ru), with the square-planar and octahedral geometries about the respective metals. Unfortunately, attempts to obtain X-ray quality crystals of **10** and **11** in different solvents and by exchanging the triflate anion for BF_4^- and BPh_4^- were unsuccessful.

Addition of PMe_3 to compound **10** in attempts to displace the Os-bound ester group instead gives the product $[RhOs(CO)_2(PMe_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2C(CO_2Et)_2)(dppm)_2][CF_3SO_3]$ (**13**), the structure of which is diagrammed below, via substitution of a carbonyl. The ^{31}P NMR spectrum of this product exhibits three multiplets of 2:2:1 intensity ratio at δ 28.4, 12.1, and −18.5. The low-field signal, being the AA′ portion of an AA′BB′CX spin system, corresponds to the Rh-bound phosphorus nuclei of the dppm ligand, clearly evident by its strong coupling to the Rh nucleus ($^1J_{RhP}$ = 162 Hz) and additional coupling to the other phosphines of the dppm bridge as well as to the PMe_3 ligand, whereas the signal at δ 12.1 (the BB′ portion) corresponds to the Os-bound phosphines of the dppm ligand on the basis of its higher-field chemical shift and absence of Rh coupling. Finally, a doublet of triplets at δ −18.5 is assigned to the PMe_3 ligand and shows strong coupling to both the Rh-bound phosphines of the dppm ligands ($^2J_{PP}$ = 42 Hz) and the Rh nucleus ($^1J_{RhP}$ = 129 Hz) to which it is bound. This clearly establishes that coordination of PMe_3 to Rh and not to Os has occurred. A solution of compound **13** was monitored over a period of two weeks by ^{31}P NMR spectroscopy, and no further transformations were observed. Again, attempts to obtain X-ray quality crystals of **13** failed. Interestingly, the IR spectrum of **13** shows ester stretches at 1752 and 1686 cm^{-1}, more in line with structure **C** and with that of the Rh/Ru species **11**.



(13)

Treatment of compound **1** with $N_2CHSiMe_3$ (TMSDM) also leads to a carbonyl-substitution product, $[RhOs(CO)_3(N_2CHSi(CH_3)_3)(dppm)_2][CF_3SO_3]$ (**12**), again containing the intact diazoalkane group, as confirmed by elemental analysis. In addition, the mass spectrometry fragmentation pattern observed strongly suggests a product in which the intact diazoalkane group is present, showing peaks associated with the loss of both the $CHSiMe_3$ and $N_2CHSiMe_3$ fragments. The formation of compound **12** is accompanied by the formation of numerous unknown silane products, presumably from the decomposition of TMSDM. Furthermore, this product is unstable, even in the solid state, decomposing over several hours into an oily residue composed of a complex mix of unknown products, limiting our characterization of **12**. In the $^{13}C\{^1H\}$ NMR spectrum two carbonyl resonances are observed in a 2:1 intensity ratio. The latter appears as a doublet of multiplets at δ 181.2 with coupling to the pair of Rh-bound ^{31}P nuclei and to ^{103}Rh ($^1J_{RhC}$ = 80.3 Hz), establishing that it is terminally bound to this metal, while the other resonance, at δ 194.6, appears as a doublet of multiplets of double intensity and displays coupling to the Os-bound phosphines, as well as weak coupling to the ^{103}Rh nucleus of 3.3 Hz. The lower-field resonance for the Os-bound carbonyls is consistent with these groups being bound primarily to Os but having a weak semibridging interaction with Rh,[66,72] a formulation that is supported by the small Rh−C coupling observed. However, the IR spectrum, which shows two terminal (ν(CO) = 2059, 1977 cm^{-1}) and one bridging CO stretch (1804 cm^{-1}), suggests a slightly different interpretation in which one Os-bound carbonyl is terminally bound while the other is semibridging, as diagrammed earlier in Scheme 2 (a classical bridging carbonyl is ruled out on the basis that the averaged $^1J_{RhC}$ would be higher than the 3.3 Hz observed). Facile exchange of these carbonyls between the terminal and semibridging positions is rapid on the NMR time scale and probably involves the movement of only a few tenths of an angstrom. As a consequence, only the average signal is seen in the $^{13}C\{^1H\}$ NMR spectrum, even at −80 °C, whereas the faster time scale of the IR experiment allows both the bridging and terminal stretches to be observed. Similar dynamics have been reported previously in related species.[56b,79] The four dppm methylene protons are equivalent on the NMR time scale, appearing as a single multiplet at δ 4.03, even at −80 °C, indicating the same average chemical environment on each side of the $RhOsP_4$ plane. This suggests that the diazoalkane is bound in a linear or close-to-linear manner in the site opposite the Rh−Os bond; any other site would result in the loss of symmetry about the $RhOsP_4$ plane, resulting in the chemical inequivalence of the two pairs of dppm methylene protons. In addition, occupation of any other

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(78) Woodcock, C.; Eisenberg, R. *Organometallics* **1985**, *4*, 4.

(79) Ristic-Petrovic, D.; Anderson, D. J.; Torkelson, J. R.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Organometallics* **2005**, *24*, 3711.

site on the Os center by the TMSDM ligand would not allow the facile carbonyl exchange noted above. Linearly bound diazoalkane ligands are well documented.[10,12] The structure proposed is similar to those reported previously, for the symmetric isomer of the monoethylene and bis-ethylene compounds [RhOs(CO)$_3$(η^2-C$_2$H$_4$)(dppm)$_2$][BF$_4$] and [RhOs(CO)$_2$(η^2-C$_2$H$_4$)$_2$(dppm)$_2$][BF$_4$], respectively, which have similar symmetries with respect to the pair of Os-bound carbonyls. Consistent with the proposal of similar structures, the spectral parameters for these ethylene complexes are closely comparable to those of **12**.[56b] In particular, the Os-bound carbonyls for these two ethylene adducts appear at δ 198.0 ($^1J_{\mathrm{RhC}} = 6$ Hz) and 195.5 ($^1J_{\mathrm{RhC}} = 6$ Hz), respectively, in the ^{13}C{^{1}H} NMR spectra, very close to the low-field resonances of **12**.

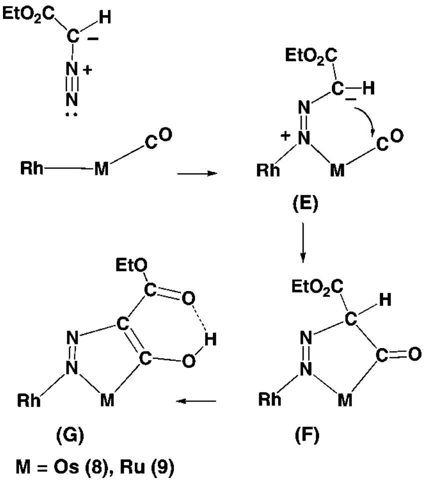
Attempts to generate the Rh/Ru analogue of **12**, namely, [RhRu(CO)$_3$(N$_2$CHSiMe$_3$)(dppm)$_2$][CF$_3$SO$_3$], failed, giving either no reaction or uncharacterized decomposition products, depending on the reaction conditions.

Having the series of metal-bound diazoalkanes in which these ligands were either bridging the pairs of metals (compounds **8**−**11**) or terminally bound to one (compound **12**), we were interested in determining whether these coordination modes activated these ligands toward N$_2$ loss. However, photolysis or subjecting compounds **8**−**11** to reflux in a number of solvents, even for extended periods, did not induce N$_2$ loss, leaving the complexes unchanged. Compound **12** decomposed to unidentified products under these conditions, as described earlier.

Discussion

(a) Methylene and Alkylidene Coupling. Although the reaction of [RhOs(CO)$_4$(μ-CH$_2$)(dppm)$_2$][X] (**3**) with diazomethane is facile at temperatures above −50 °C, yielding C$_3$ or C$_4$ fragments coordinated to the metals,[56,63] the analogous reactions of **3** with the substituted diazoalkanes N$_2$CRR′ (R = H, R′ = CO$_2$Et, SiMe$_3$; R = R′ = CO$_2$Et) are extremely slow even at ambient temperature. Furthermore, in these latter reactions no metal-bound hydrocarbyl fragments are observed and after several days only the olefins that correspond to coupling of the bridging methylene group and the diazoalkane-generated alkylidene fragment, together with compound **1** and decomposition products, are observed. Carrying out the reactions at low temperature only serves to slow the reactions further, without allowing the observation of reaction intermediates. The Rh/Ru analogue (**4**) reacts similarly. However, the same reactions using the tricarbonyl complexes [RhM(CO)$_3$(μ-CH$_2$)(dppm)$_2$][X] (M = Os (**5**), Ru (**6**)) are almost immediate at ambient temperature, again yielding the free olefins and (where identified) the same metal-containing products. If the reaction involving **5** and EDA (N$_2$CHCO$_2$Et) is carried out at −20 °C, an olefin-containing species, [RhOs(CO)$_3$(η^2-H$_2$C═C(H)CO$_2$Et)(dppm)$_2$][X] (**7**), is observed as diagrammed in Scheme 1. This product has resulted from coupling of the methylene and alkylidene fragments at the adjacent metals. This olefin complex does not have a targeted olefin-bridged structure; instead this group appears to be terminally bound to Os. Furthermore, unlike the ethylene analogue prepared by the reaction of **5** with diazomethane, which is stable upon warming to ambient temperature,[56b] compound **7** readily undergoes loss of ethyl acrylate at temperatures above −20 °C. We assume that the greater lability of **7** compared to its ethylene analogue results from unfavorable steric interactions involving the dppm phenyl groups and the bulky CO$_2$Et group. The olefin adducts, analogous to **7**, involving the larger SiMe$_3$ substituents (from TMSDM) and the two CO$_2$Et substituents (from DEDM) are even less stable than **7**, appearing in only small quantities relative to decomposition products at temperatures below −20 °C. In the case of the Rh/Ru analogues, no olefin adduct is observed down to −80 °C, even for ethyl acrylate, presumably owing to the weaker olefin binding to Ru compared to Os.[80]

Scheme 3



(b) Diazoalkane and Related Complexes. Attempts to generate substituted alkylidene-bridged analogues of compounds **3** and **4**, by the reactions of **1** and **2**, respectively, with a series of diazoalkanes, also did not yield the targeted products. Instead an interesting series of complexes have been generated in which the “NNC” moiety of the diazoalkane precursors has remained intact. Of the three different diazoalkanes investigated, the most surprising result involves EDA, in which coordination in the bridging site is accompanied by condensation of the diazoalkane carbon and an adjacent carbonyl group with subsequent hydrogen transfer from this diazoalkane to the carbonyl oxygen, yielding an enolate moiety. Formation of a metallacyclic-enol product from a metal-carbonyl precursor suggests the involvement of a keto−enol tautomerization[81] step. This proposal is outlined in Scheme 3 (ancillary ligands omitted), in which reaction of ethyl diazoacetate with the “RhM(CO)$_4$” fragment is proposed to first yield the diazoalkane-bridged intermediate (**E**), similar to other diazoalkane-bridged complexes.[40–43] Nucleophilic attack of the diazoalkane carbon at the carbonyl ligand would yield the metallacycloketone (**F**), which could then tautomerize to the metallacyclic enol (**G**). This enol product is presumably stabilized by conjugation between the olefinic double bond and both the diazo and the ester carbonyl functionalities and also by the hydrogen bond between the enol and ester carbonyl group. Reactions of the very analogous homobinuclear complexes [Rh$_2$(CO)$_2$(μ-H)$_2$(dppm)$_2$] and [Ru$_2$(CO)$_4$(μ-CO)(dppm)$_2$] with EDA did not yield metallacyclic products like **8** and **9**, but instead gave simple diazoalkane-bridged products, depicted by structure **VI**.[43,78] Although, as noted earlier, condensations involving diazoalkanes and carbonyl ligands have not been observed on a metal template, the transformations reported for **8** and **9** are reminiscent of the

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(80) (a) Li, J.; Schreckenbach, G.; Ziegler, T. *Inorg. Chem.* **1995**, *34*, 3245. (b) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092.

(81) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: Oxford, 2001.

coupling reactions involving ethyl diazoacetate and aldehydes, using a variety of catalysts..[82]

In an attempt to observe and characterize a species that would model either the diazoalkane-bridged species **E** or the metallacyclic ketone species **F**, we undertook the reactions of **1** and **2** with diethyl diazomalonate (DEDM), which lacks a hydrogen substituent on the diazoalkane carbon, ruling out the possibility of keto−enol tautomerism. This strategy has succeeded in generating a diazoalkane-bridged product, with both the Rh/Os and the Rh/Ru systems. However, in both of these cases one of the ester carbonyl groups also displaces a carbonyl ligand and binds to the group 8 metal as a dianionic, 6 e^- donor diazoalkane ligand. The failure of DEDM to yield a metallacyclic ketone similar to structure **F** (Scheme 3), which would result from coupling of the bridging diazoalkane ligand and an adjacent carbonyl ligand, may be due to the increased steric crowding in the disubstituted diazoalkane (DEDM) ligand, which inhibits approach of the diazoalkane carbon to the carbonyl ligand. The entropy increase that results from the carbonyl displacement in generating compounds **10** and **11** also cannot be overlooked as a driving force for the observed transformation.

The singly substituted TMSDM group, having hydrogen and trimethylsilyl substituents on the diazoalkane carbon, has no carbonyl oxygen with which to chelate to the group 8 metal, ruling out products analogous to compounds **10** and **11**. However it has the potential to yield a condensation product such as **F** and in principle can also undergo a tautomerization step yielding a metallacyclic enol similar to **G**. In this case, however, the absence of an ester carbonyl group means that such an enol product would have neither the stabilization of the hydrogen bond nor the stabilization resulting from conjugation involving the olefin and carbonyl functionalities that exist in **8** and **9**. In this case, however, no product containing a bridging diazoalkane group is observed. Instead the unstable product (**12**) contains a terminally bound diazoalkane ligand, as shown in Scheme 2.

In order to minimize the steric bulk of the diazoalkane, we also investigated reactions involving diazoethane ($N_2C(H)CH_3$) and compounds **1** and **2**. Surprisingly, no reaction involving this diazoalkane and these compounds was observed between −80 °C and ambient temperature. We certainly observed the formation of both *cis*- and *trans*-butene, under the conditions investigated; however, these olefins were also obtained under the same conditions in the absence of compounds **1** and **2**, so their formation was not metal-mediated.

(c) Comparisons of N_2CH_2 and N_2CRR'. The reactions of the mixed-metal complexes described above with substituted diazoalkanes and with diazomethane differ significantly. In the reactions involving the methylene-bridged Rh/Os complexes **3** and **5**, all diazoalkanes (including N_2CH_2) initially behave similarly, resulting in coupling of the bridging methylene group with the alkylidene fragment of the diazoalkane. However, whereas diazomethane reacted with **3** to give multiple methylene couplings, the substituted diazoalkanes give rise to olefins arising from coupling of an alkylidene fragment with the metal-bound methylene group. We suggest that this may be a consequence of steric factors that labilize the substituted olefins, first forcing them out of the bridging site, where methylene coupling is proposed to occur in this system,[56b,63] and subsequently leading to olefin loss.

Whereas the methylene-bridged Rh/Ru complex (**4**)[58] had behaved very differently than its Rh/Os analogue[56] in failing to react further with diazomethane, this complex did react with the substituted diazoalkanes, yielding olefins, paralleling the chemistry observed with Rh/Os. In both cases, the methylene-bridged tricarbonyls were much more reactive than the tetracarbonyl analogues.

In the reactions of diazoalkanes with the tetracarbonyl complexes $[RhM(CO)_4(dppm)_2][X]$ (M = Ru (**2**), Os (**1**)), the difference between the prototype (N_2CH_2) and the substituted diazoalkanes studied is even more pronounced. With diazomethane, no species was ever observed containing the intact N_2CH_2 ligand; instead N_2 extrusion was extremely facile (occurring even at −80 °C), generating methylene groups and other hydrocarbyl ligands formed from methylene-group condensations. In contrast, the substituted diazoalkanes (with the exception of diazoethane, which failed to react) formed only diazoalkane complexes or related species and could not be induced to undergo N_2 loss when heated or photolyzed. Milstein, Martin, and co-workers have argued convincingly that "...an important requirement for the carbene formation is the viability of and η^1-C coordinated diazo complex" and have shown that the viability of this key intermediate is largely determined by steric factors;[13] the greater the steric demand of the diazoalkane substituents, the less favorable will be this pivotal intermediate. In support of these ideas, our only observation of carbene formation is with unsubstituted diazomethane. Coordination of the diazoalkane or related moiety through the terminal nitrogen, in a bridging (compounds **8**−**11**) or terminal η^1-N mode (compound **12**), does not lead to carbene formation, even under forcing conditions.

Finally, it seems puzzling that coordination of diazoalkane is observed in reaction of **1** and **2**, *with no alkylidene formation*, yet alkylidene formation clearly occurs at some stage in reactions involving the more crowded methylene-bridged complexes **3**−**6**, since the corresponding olefins ($CH_2{=}CRR'$) are obtained, through coupling of the methylene fragment with the diazoalkane-generated alkylidene fragment. It appears unlikely that in these reactions the requisite η^1-C coordinated diazoalkane complex can be accessed to allow alkylidene formation for subsequent coupling with the bridging methylene group, since such reactivity was not observed for the less crowded complexes **1** and **2**. For this reason, we propose that coupling of the intact diazoalkane ligand and the methylene group may occur prior to N_2 extrusion, instead of the opposite pathway, although we have no evidence of diazoalkane coordination prior to olefin formation.

Conclusions

Although our efforts to generate substituted C_1- and C_2-bridged species through the use of substituted diazoalkanes were not successful, we were able to characterize an interesting, unstable ethyl acrylate complex, resulting in the coupling of an ethyl diazoacetate-generated alkylidene and the metal-bridging methylene group. It appears that our failure to generate the targeted species is largely a result of steric influences of the diazoalkane substituents; generation of the η^1-C coordinated diazoalkanes as prerequisites to the targeted bridging alkylidene species appears to be inhibited by the bulk of the diazoalkane substituents, and the olefin-bridged targets appear to be unstable, again for steric reasons. However, in our unsuccessful attempts to generate alkylidene-bridged products we were able to generate three interesting and rather different complexes that involve incorporation of the intact "NNC" part of diazoalkane molecules,

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[82] (a) Evans, D. A.; Truesdale, L. K.; Grimm, K. G. *J. Org. Chem.* **1976**, *41*, 3335. (b) Yao, W.; Wang, J. *J. Org. Chem.* **2003**, *5*, 1527. (c) Xiao, F.; Liu, Y.; Wang, J. *Tetrahedron Lett.* **2007**, *48*, 1147. (d) Kantam, M. L.; Balasurbrahmanyam, V.; Kumar, K. B. S.; Venkanna, G. T.; Figueras, F. *Adv. Synth. Catal.* **2007**, *349*, 1887.

adding further to the interesting coordination chemistry of these species. Unlike our previous studies involving diazomethane, for which the Rh/Ru and Rh/Os metal combinations displayed very different reactivities, both metal combinations reacted quite analogously with the substituted diazoalkanes studied.

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Supporting Information Available: CIF file giving crystallographic details for compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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