ORGANOMETALLICS

Reaction of the (trimethylsilyl)diazomethane anion with metal complexes: synthesis and x-ray study of iodomethyltris(trimethylphosphine)rhodium(III) (trimethylsilyl)diazomethane, RhICH3(PMe3)3{C(N2)SiMe3}

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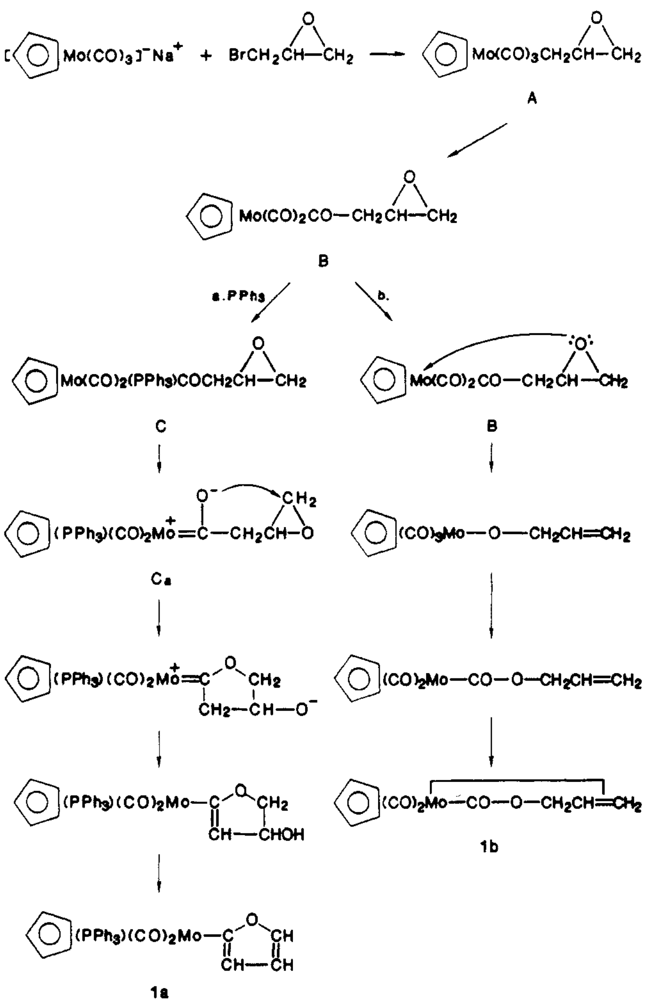
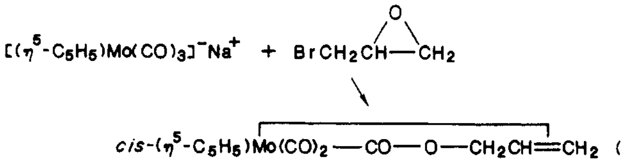
Scheme I



into tetrahydrofurans.[4] In this process an intramolecular attack by the C=O group of the acetate upon the epoxide ring is the key step, and the mechanism we suggest for the complex formation is outlined in Scheme Ia. This involves the initial formation of a σ-bonded epoxymethyl complex A, followed by migratory CO insertion to produce the 16e coordinatively unsaturated complex B. This may be trapped by the phosphine to form C which contains a very nucleophilic acyl group by virtue of the contributing resonance structure C_a. We suggest this group participates in an intramolecular attack to yield the ultimately isolated furan complex. A previous example of an intramolecular attack by a metal acyl group due to its nucleophilicity is provided by the isolation of a cyclic cationic carbene complex upon treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)_3Br$ with PPh_3.[5]

Support for the proposed mechanism was obtained from the reaction of the molybdenum carbonylate and epibromohydrin in the absence of triphenylphosphine (eq 2). In this reaction no furan ring was formed and a different intramolecular rearrangement involving CO incorporation took place.

This result shows the importance of trapping the 16e complex B by PPh_3 (Scheme Ia). In the absence of this ligand, the O atom of the epoxide interacts with the electron-deficient Mo atom, probably to form a transient allyloxy complex which upon rapid migratory CO insertion



(2)

will form the isolated σ–π complex (Scheme Ib).[6] If triphenylphosphine is added to a reaction mixture of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+$ and epibromohydrin, only the σ–π complex is isolated. Furthermore, thermal (refluxing THF solution) or photochemical treatment of the σ–π complex with PPh_3 leads to the isolation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(PPh_3)]$.[7] These reactions preclude the intermediacy of the σ–π complex in the formation of the furan complex.

Extension of this new chemistry to oxiranes, episulfides, and related ring systems along with formation of variously substituted furans is currently in progress.

Acknowledgment. Support of this research by the Robert A. Welch Foundation, Houston, TX, and by a Texas Advanced Technology Research Award is gratefully acknowledged. Financial support and leave of absence to R.C.-O. from the Instituto de Quimica, UNAM, are also acknowledged.

Supplementary Material Available: Tables of crystal data, atom coordinates, bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates (6 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(6) The reaction was performed on the same scale, in the same manner, as that in the presence of triphenylphosphine to yield 0.85g (2.8 mmol, 74%) of the σ–π complex. Elution of the column with a 40:60 hexane/CH_2Cl_2 solvent mixture removed any $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ formed, and the product was eluted with CH_2Cl_2: orange solid; mp 95 °C darkens, 112–113 °C dec. Anal. Found (Calcd): C, 44.1 (43.7); H, 3.45 (3.31). IR: ν(CO) (CH_2Cl_2), 2012 (s, 1949 (s, bd), 1646 (m) cm^{-1}. NMR (ppm, C_6D_6): ^{13}C, 235.2 (CO), 228.4 (CO), 215.3 (Mo-CO-O), 93.1 (C_5H_5), 79.3 ($CH_2=CH$), 65.7 ($CH_2=CH$), 31.8 (CH_2); ^1H, 2.14 (d, J = 3.8 Hz, Mo-CO-O-CH_aH_b), 2.36 (d, J = 6.5 Hz, Mo-CO-O-CH_aH_b), 3.89 (m, $CH=CH_aH_b$), 4.41 (d, J = 5.9 Hz, $CH=CH_aH_b$), 4.84 (C_5H_5).

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Reaction of the (Trimethylsilyl)diazomethane Anion with Metal Complexes: Synthesis and X-ray Study of Iodomethyltris(trimethylphosphine)rhodium(III) (Trimethylsilyl)diazomethane, $RhICH_3(PMe_3)_3\{C(N_2)SiMe_3\}$

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Summary: $LiC(N_2)SiMe_3$ reacts with $Rh(PMe_3)_4Cl$ at low temperature to give $Rh\{C(N_2)SiMe_3\}(PMe_3)_4$ (**1**) in high yield. This complex adds MeI oxidatively in benzene to give orange $Rh\{C(N_2)SiMe_3\}MeI(PMe_3)_3\cdot C_6H_6$ (**2**). **2** crystallizes in the space group *Pnma*, with a = 9.352 (1) Å, b = 10.916 (2) Å, c = 29.358 (5) Å, Z = 4, and V = 2997 $Å^3$. Controlled thermolysis generates several rhodium species, of which $RhI(Me)_2(PMe_3)_3$ has been isolated as the final product.

Diazoalkanes are versatile reagents in organic[1] and in organometallic[2] chemistry where they are important precursors for carbene synthesis. A number of α heavier main-group-element diazo derivatives are known,[3] but, in contrast, very few C-substituted diazoalkane transition-metal compounds have been isolated. Carbonyl and cyclopentadienyl metal complexes have been reported to catalyze their decomposition, which probably explains why, to our knowledge, only $PdX(CN_2R)(PR_3)_2$, $Pd(CN_2R)_2(PR_3)_2$,[4] and $OsClI(NO)(CN_2CO_2Et)(PPh_3)$[5] have been characterized. In this paper, we report the synthesis and characterization of the first diazo moiety substituted both by a transition metal and a heavier main-group element.

(Trimethylsilyl)diazomethanerhodium(I), **1**, can be prepared by treating tetrakis(trimethylphosphine)rhodium(I) chloride[6] with the lithium salt of (trimethylsilyl)diazomethane.[7]

$$\mathrm{Rh(PMe_3)_4Cl + LiC(N_2)SiMe_3 \rightarrow \underset{\mathbf{1}}{Rh(PMe_3)_4\{C(N_2)SiMe_3\}} + LiCl}$$

Compound **1** cannot be isolated in analytically pure form. Decomposition is observed in the solid state or in solution after a few days. Both ^1H and ^{31}P NMR show a single broad peak at room temperature for phosphines,[8] indicating fluxional behavior. The 173 K $^{31}P\{^1H\}$ NMR is a sharp doublet at −4 ppm in C_7D_8 with $J_{Rh-P} = 140$ Hz. This observation provides evidence either for a square-pyramidal molecule, the only possible structure with four equivalent phosphines, or for a fluxional trigonal-bipyramidal species.[9] The most striking characteristic of the coordinated diazo group is the intense band at 1950 cm^{-1} in the infrared spectrum. It is considerably shifted to lower frequencies, compared to diazoalkanes, as already noted for the other known α-diazo transition-metal complexes.[4,5]

Complex **1** rapidly and quantitatively reacts with methyl iodide to give the rhodium(III) diazo complex **2**, which can be isolated in analytically pure form.

$$\mathrm{\mathbf{1} + 2MeI \rightarrow \underset{\mathbf{2}}{RhIMe(PMe_3)_3\{C(N_2)SiMe_3\}} + [Me_4P]I}$$

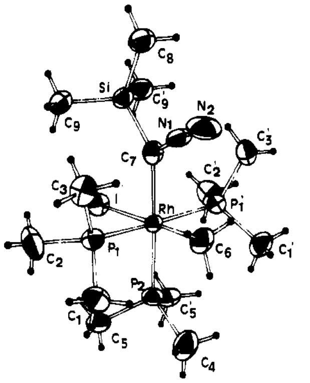

Figure 1. Structure of $Rh\{C(N_2)SiMe_3\}MeI(PMe_3)_3 \cdot C_6H_6$. Selected bond lengths (Å): Rh–I, 2.808 (2); Rh–P(1), 2.322 (6); Rh–P(2), 2.339 (4); Rh–C(6), 2.10 (2); Rh–C(7), 2.10 (2); C(7)–Si, 1.91 (2); C(7)–N(1), 1.30 (3); N(1)–N(2), 1.09 (3). Bond angles (deg): P(1)–Rh–P(2), 93.6 (1); P(1)–Rh–I, 94.9 (2); P(2)–Rh–I, 94.9 (1); C(6)–Rh–I, 179.3 (7); C(7)–Rh–I, 92.2 (6); C(6)–Rh–P(1), 94.4 (7); C(6)–Rh–P(2), 85.1 (1); C(7)–Rh–P(1), 86.6 (1); C(7)–Rh–P(2), 177.1 (6); C(7)–Rh–C(6), 88.5 (9); Rh–C(7)–N(1), 119 (2); Rh–C(7)–Si, 134 (1); N(1)–C(7)–Si, 107 (2); C(7)–N(1)–N(2), 175 (2).

Compound **2** is stable enough to be handled briefly in air without noticeable decomposition. The spectral data are in agreement with the proposed structure. A strong infrared band at 1955 cm^{-1} confirms the presence of the diazo group. ^1H NMR shows two phosphines mutually trans and another cis, as well as a singlet for the trimethylsilyl group and a doublet of doublets of triplets for the methyl group. The $^{31}P\{^1H\}$ at 99 MHz indicates the expected doublet of doublets and doublet of triplets.[10]

Recrystallization of **2** in benzene affords orange-red crystals of the benzene adduct, suitable for crystal structure determination. The X-ray diffraction study[11] shows that it consists of monomeric molecules, as illustrated in Figure 1 along with the atom numbering scheme and a summary of pertinent metric parameters. The rhodium atom is at the center of a distorted octahedron. The diazo ligand is planar and lies in the equatorial plane, defined by the Rh, C(6), C(7), I, and P(2) atoms which lie on the crystallographic mirror plane. This ground-state geometry is presumably sterically favored; a twist of the diazoalkane about the Rh–C(7) axis would lead to an unfavorable interaction between $SiMe_3$ and PMe_3 groups. Electronic effects resulting from interaction of the π and π^* sets of orbitals of the diazoalkane and the rhodium(III) d orbitals may also be operative,[4] although the similar values observed for the Rh–Me and Rh–CN_2SiMe_3 distances suggest that π bonding involving rhodium is not appreciable. The sp^2 hybridization of the diazo carbon atom is apparent from the Rh–C(7)–N(1), Rh–C(7)–Si, and N(1)–C(7)–Si angle values and the linearity of the CN_2 group (175 (2)°). The N–N bond length (1.09 (3) Å) is remarkably short

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(10) NMR: ^1H (C_6D_6), δ 1.21 (dd, 9 H, $J_{HP} = 8$ Hz, $J_{HRh} = 0.6$ Hz, PMe_3), 1.31 (dt, 18 H, $J_{HP} = 3$ Hz, $J_{HRh} = 0.6$ Hz, PMe_3), 0.81 (s, 9 H, $SiMe_3$), 0.17 (ddt, 3 H, $J_{HP_a} = 7$ Hz, $J_{HP_e} = 3.7$ Hz, $J_{HRh} = 2$ Hz, CH_3); ^{31}P (C_6D_6): δ −9 (dd, $J_{PRh} = 99$ Hz, $J_{PP} = 32$ Hz, P_a), −20 (dt, $J_{PRh} = 97$ Hz, $J_{PP} = 32$ Hz, P_e).

(11) Crystal data: Diffractometer data (5078) were measured at room temperature on an Enraf-Nonius CAD-4 diffractometer by $\theta/2\theta$ scan with Mo Kα radiation up to $\theta = 31°$, of which 2190 were used ($I > 3\sigma(I)$). **2**: orthorhombic; space group *Pnma*; $Z = 4$; $a = 9.352$ (1) Å, $b = 10.916$ (2) Å, $c = 29.358$ (5) Å; $V = 2997$ Å^3; μ(Mo Kα) = 16.61 cm^{-1}, $T = 20$ C°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques as already reported. All non-hydrogen atoms were refined anisotropically including anomalous dispersion effects. The hydrogen atoms were introduced in idealized positions (*Inorg. Chem.* **1986**, *25*, 1383). Full-matrix least-squares refinement broke down only to $R = 0.067$ ($R_w = 0.088$) certainly because of the thermal agitation of the CN_2 group.

compared to that obtained in diazoalkanes,[1,12] but such values have already been observed in metal–nitrogen complexes and are a consequence of the thermal vibration of the nitrogen atoms.[13] MeI adds oxidatively trans, as usual in nonpolar solvent.[14]

Note that $LiC(N_2)SiMe_3$ does not react with $RhCl(PPh_3)_3$, but it is still not known whether steric or electronic effects are dominant. Thermolysis or photolysis of 2 gives rise to several rhodium species of which $RhIMe_2(PMe_3)_3$[15] is the major product.

In conclusion, the synthetic preparative method commonly used to prepare the rhodium methyl species can be extended to diazomethane complexes. Work is now in progress to study the extension of this result to other metals and to other α heavier main-group-element diazo ligands.

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Supplementary Material Available: Tables of refined temperature factors, final fractional coordinates, and fixed coordinates of the hydrogen atoms (3 pages); a listing of observed and calculated structure factors amplitudes (6 pages). Ordering information is given on any current masterhead page.

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[15] Thorn, D. L. *Organometallics* **1985**, *4*, 192. The yield of $RhI(Me)_2(PMe_3)_3$ depends on the reaction conditions and especially on the solvent. It is higher than 50% in $CDCl_3$. Experiments are now in progress to determine the origin of the second methyl group. Two other rhodium complexes have been characterized by phosphorus NMR (A_2B spectrum) during the thermolysis, but not isolated. The trimethylsilyl substituent is involved in the thermolysis process, and work is going on to determine the nature of the resulting silyl species.

A Tris-Chelating Oxygen Ligand Stabilizing the $W_2(CO)_4(W{\equiv}W)$ Fragment. Synthesis and Crystal Structure of $L_2W_2(CO)_4$ ($L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$)

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Summary: From the reaction of $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$ (NaL) with $W(CO)_6$ in refluxing diglyme the dark red crystalline compound $[L_2W_2(CO)_4]$ has been obtained. The crystal structure determination shows that the tris-chelating oxygen ligands L^- coordinate each to one tungsten center. The four carbonyls are bent back over the tungsten–tungsten triple bond to form linear-type asymmetric bridges. NMR and IR data indicate that the solid-state structure is retained and is relatively rigid in solution.

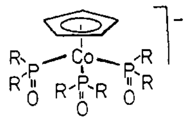

Figure 1. Schematic representation of the oxygen tripod ligand L^- ($R = OC_2H_5$).

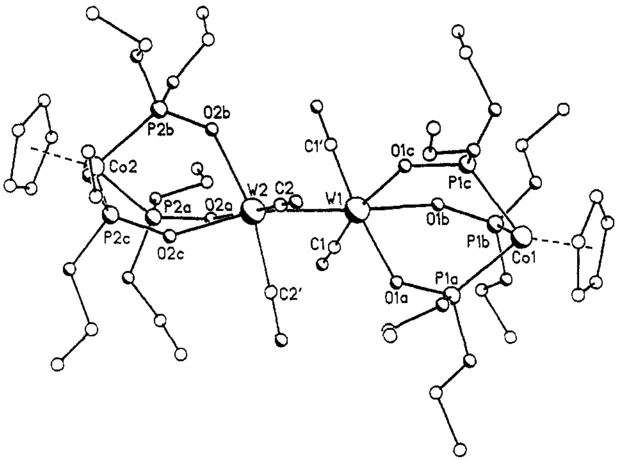

Figure 2. Crystal structure of $[L_2W_2(CO)_4]$ ($L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$).

The anion (cyclopentadienyl)tris(diethyl phosphito)cobaltate(1−), hereafter abbreviated as L^-, has a strong tendency to act as an O,O,O-tripod ligand by using the oxygen atoms of the three $R_2P{=}O$ functional groups as donor centers (see Figure 1). It forms stable complexes with metal ions in high as well as in low oxidation states.[1] We have recently observed that the metal(0) complexes $[LM(CO)_3]^-$ (M = Cr, Mo, W)[2] are useful starting compounds for the synthesis of a variety of hydride and alkyl complexes $[LM(CO)_3R]$ (R = H, alkyl) and of nitrosyl and allyl complexes $[LM(CO)_2R']$ (R' = NO, η^3-allyl). No other oxygen ligands are known to stabilize such a broad range of organometallic fragments.[3] It seemed therefore interesting to further explore the organometallic chemistry of this ligand. We have now prepared the tungsten–tungsten triply bonded dimer $[L_2W_2(CO)_4]$, the first metal complex of L containing a multiple metal–metal bond. It may be noted that the only other complexes containing the $W_2(CO)_4$ unit are the cyclopentadienyl complexes $[(C_5R_5)_2W_2(CO)_4]$ (R = H,[4] CH_3[5]). Of the various attempts to synthesize the title compound according to the synthesis of the analogous complexes $[(C_5R_5)_2M_2(CO)_4]$, neither thermolysis or photolysis nor aerial oxidation of $[LW(CO)_3H]$ has led, in our hands, to $[L_2W_2(CO)_4]$. This compound is, however, accessible in one step in moderate yields from NaL and hexacarbonyl tungsten in refluxing diglyme.[6] A crystal structure determination[7] revealed the

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