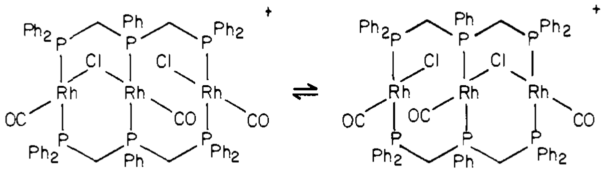
the temperature range +25 to −70 °C. To account for the equivalence of all four of the terminal phosphorus atoms, we propose that, in solution, the chloride ligands undergo rapid bridge–terminal exchange as shown in eq 1. This operation requires only minimal geometric displacements of the carbonyl group on Rh(2) and the chloride ligands. Note that the nonbonded Rh(2)···Cl(2) separation is only 1.087 Å longer than the Rh(2)–Cl(1) bond length.



(1)

Preliminary results indicate that $[(\mu\text{-dpmp})_2Rh_3(\mu\text{-Cl})Cl(CO)_3]^+$ has a rich reaction chemistry. Adducts are readily formed with sulfur dioxide and activated acetylenes. Although **3** readily and reversibly adds carbon monoxide in the trough between the two rhodium centers to form the double A-frame, $[(\mu\text{-dpm})_2Rh_2(\mu\text{-CO})(\mu\text{-Cl})(CO)_2]^+$,[10] carbon monoxide (at 1 atm) does not add to the similarly sized trough in **2**.

Acknowledgment. We thank the National Science Foundation (CHE 7924575) for support. Acquisitions of the X-ray diffractometer and NMR spectrometer used in these studies were made possible through NSF equipment grants.

Registry No. 1, 84751-01-9; $\mathbf{2}^+Cl^-\cdot CH_2Cl_2$, 84751-03-1; $\mathbf{2}^+BPh_4^-$, 84774-75-4; $\mathbf{2}^+PF_6^-$, 84774-76-5; bis(benzonitrile)palladium(II) chloride, 14220-64-5; dicarbonylrhodium(I) chloride dimer, 14523-22-9.

Supplementary Material Available: List of atomic fractional coordinates and thermal parameters for $(dpmp)PdCl_2\cdot CH_2Cl_2$ and $[(\mu\text{-dpmp})_2Rh_3(\mu\text{-Cl})Cl(CO)_3]Cl\cdot 1.5C_2H_2Cl_4$ and the $^{31}P\{^1H\}$ NMR spectrum of **2** (4 pages). Ordering information is given on any current masthead page.

Preparation and Reactivity of a Dimeric Ruthenium μ-Methylene Complex with No Metal-Metal Bond: Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2(\mu\text{-}CH_2)$

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Transition-metal methylene complexes have attracted attention because of their proposed role in catalytic reactions and their novel structural and chemical features.[1] All known bridging methylene complexes contain either a metal–metal bond or an additional bridging ligand.[2] Indeed, it has been postulated that these are necessary structural features to stabilize μ-methylene complexes.[1] Here we report the isolation and characterization of a methylene complex without these features. We have found that this compound is far more reactive than analogous alkyl or metal–metal bonded μ-methylene complexes; for example, it readily inserts CO, affording a complex containing the $RuC(O)CH_2Ru$ fragment.

The μ-methylene complex $[CpRu(CO)_2]_2(\mu\text{-}CH_2)$ (**1**) was prepared by reacting $Na[CpRu(CO)_2]$ with 0.5 equiv of methylene chloride at −35 °C in THF and isolated by warming the reaction mixture to room temperature, evaporating the solvent, and recrystallizing from hexane (eq 1).[3] The complex decomposes at room temperature over a 24 h period but can be kept indefinitely at −35 °C. Use of $CH_2(OTs)_2$ instead of CH_2Cl_2 gave **1** in lower yield.

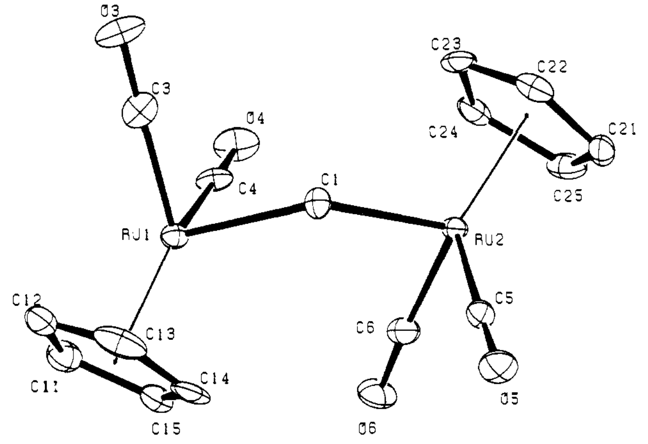
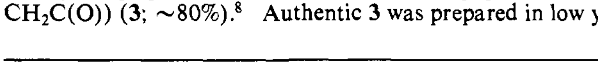


Figure 1. ORTEP drawing of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2(\mu\text{-}CH_2)$. The vibrational ellipsoids are drawn at the 50% probability level.

$$\mathrm{Na[CpRu(CO)_2]} + {}^1/_2\mathrm{CH_2Cl_2} \rightarrow {}^1/_2\underset{\mathbf{1}}{\mathrm{Cp(CO)_2Ru(CH_2)Ru(CO)_2Cp}} \quad (1)$$

The structure[4] of **1** in Figure 1 shows that the two ruthenium atoms are symmetrical about the μ-CH_2 group. The Ru–C distance of 2.18 Å (av) is slightly longer than those in $[CpRu(CO)]_2(\mu\text{-CO})(\mu\text{-CHCH}_3)$ (2.08 Å) and $[CpRu(CO)]_2[\mu\text{-C}(CH_3)_2][\mu\text{-C}(CH_3)_2]$ (2.11 Å).[5] In these complexes, however, the Ru–Ru distance of 2.7 Å and the ∠Ru–C–Ru of 80° indicate a metal–metal bond. In **1**, which lacks this bond, the Ru–Ru distance is 3.8 Å (av) and the ∠Ru–C–Ru is 123°. This metal–metal separation is greater than that found in $[Pt_2Cl(CH_2PPh_3)](\mu\text{-dppm})_2(\mu\text{-}CH_2)$.[2a] The ∠Ru–C–Ru is somewhat larger than expected for the sp^3 hybridization. This large angle and relatively long Ru–C distance suggests steric crowding about the methylene group, which may be responsible for its unusual reactivity.

Photolysis of **1** gave an 80% yield of the cis and trans isomers of the metal–metal bonded μ-methylene dimer $[CpRu(CO)]_2(\mu\text{-}CH_2)(\mu\text{-CO})$ (**2**), previously prepared from $(Ph)_3P{=}CH_2$ and $[CpRu(CO)]_2(\mu\text{-CO})(\mu\text{-C(O)C}_2(Ph)_2)$.[6] A similar decarbonylation with concomitant metal–metal bond formation occurs for $[CpFe(CO)_2]_2[\mu\text{-Si(H)(CH}_3)]$.[7] Carbonylation of **1** occurs readily (40 psig at room temperature) to give $[CpRu(CO)_2]_2(\mu\text{-}CH_2C(O))$ (**3**; ~80%).[8] Authentic **3** was prepared in low yield



(2)

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† Contribution No. 3160.

(1) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

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(3) ^1H NMR (C_6D_6) δ 4.80 (10 H, s), 2.30 (2 H, s); ^{13}C NMR (CD_2Cl_2) δ 203.50 (CO), 90.41 (C_5H_5, $J_{C\text{-}H} = 177.9$ Hz, $J_{C\text{-}H'} = 6.8$ Hz), −37.42 (CH_2, $J_{C\text{-}H} = 137.2$ Hz). Anal. Calcd (found): C, 39.30 (39.24); H, 2.62 (2.75).

(4) Crystal data for $Ru_2C_{15}H_{12}O_4$: monoclinic, $P2/c$, $a = 19.020$ (3) Å, $b = 6.239$ (1) Å, $c = 20.046$ (4) Å, $\beta = 108.63$ (1)°, $V = 2254.1$ Å^3, ρ (calcd) = 2.026 g/cm^3, $Z = 6$, $\mu = 19.834$ cm^{-1}, crystal faces ±[100, 0.10; −102, 0.0083; −210, 0.350], 3421 reflections with $I > 2\sigma(I)$ (−100 °C), analytically corrected for absorption, 258 variables, $R = 0.058$, $R_w = 0.061$. One molecule lies in a general position while a second half molecule is related to itself by the 2-fold axis.

(5) (a) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861. (b) Cooke, M.; Davies, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *Ibid.* **1981**, 862.

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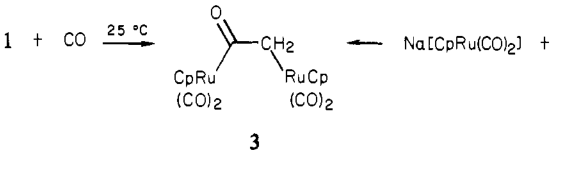
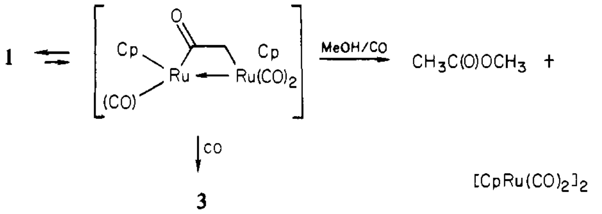
from Na[CpRu(CO)$_2$] and ClCH$_2$C(O)Cl. The bridging acyl[9] has a ν_{CO} at 1622 cm^{-1} and a ^{13}C NMR resonance at 236.7 ppm. Similarly, we find that a trimethylphosphine substituted analogue of **3**, [CpRu(PMe$_3$)(CO)](μ-C(O)CH$_2$)[CpRu(CO)$_2$] (**4**),[10] was formed from the reaction of **1** with excess PMe$_3$ at room temperature. **1** reacts with methanol and CO at room temperature, affording methyl acetate and [CpRu(CO)$_2$]$_2$. If CO is absent, methyl acetate is still formed, but **2** is produced as a byproduct. The complex Fe$_2$(CO)$_8$(μ-CH$_2$) reacts similarly.[11] Presumably, an MC(O)CH$_2$M intermediate is formed and methanolyzed in both cases. Since **3** is unaffected by methanol, we suggest that methyl acetate is formed by methanolysis of an unsaturated intermediate derived by CO insertion into the Ru–CH$_2$ bond of **1** (eq 4). Consistent with this proposal we observed that photolysis of **3** in methanol affords methyl acetate. The rapid insertion of CO into the Ru–C bond of **1** is remarkable. The Ru-alkyl derivatives CpRu(CO)$_2$CH$_2$X (X = H, OMe, OC(O)R) react only slowly with CO at 1000 psi and above 100 °C.[12]



(3)



(4)

The dimeric ruthenium complexes [CpRu(CO)$_2$]$_2$(μ-CH$_2$)$_n$ (n = 2, **5**; n = 3, **6**; n = 4, **7**) have been prepared from 1,2-dichloroethane, 1,3-dibromopropane, and 1,4-dibromobutane and Na[CpRu(CO)$_2$] for comparison.[13] These complexes are considerably more stable than **1**. When heated above 70 °C or photolyzed, **5** eliminates ethylene.[14] The complex **6** is converted to an equimolar mixture of CpRu(CO)$_2$H and CpRu(CO)(η-C$_3$H$_5$) under UV irradiation.[13b]

These observations establish that (1) μ-methylene complexes do not require metal-metal bonds or other bridging ligands for stability, (2) lack of these structural features significantly modifies reactivity, and (3) formation of methyl acetate from **1** and Fe$_2$(CO)$_8$(μ-CH$_2$) likely proceeds by methanolysis of coordinatively unsaturated intermediates containing MC(O)CH$_2$M fragments.

Acknowledgment. We thank E. A. Conaway and L. Lardear for their skilled technical assistance.

Supplementary Material Available: Summary of X-ray diffraction data (Table I), atomic positional (Table II) and thermal (Table III) parameters, bond lengths (Table IV) and bond angles (Table V), and a listing of the observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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[8] ^{1}H NMR (C$_6$D$_6$) δ 4.88 (5 H, s), 4.62 (5 H, s), 2.95 (2 H, s); ^{13}C NMR (C$_6$D$_6$) δ 202.54 (CO), 202.20 (CO), 90.42 (C$_5$H$_5$), 88.30 (C$_5$H$_5$), 27.2 (CH$_2$, J_{C-H} = 136.5 Hz), 236.70 (C=O).

[9] See, for example: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

[10] ^{1}H NMR (C$_6$D$_6$) δ 4.96 (5 H, s), 4.78 (5 H, s), 3.13 (2 H, d), 1.19 (9 H, d, J_{P-H} = 10.0 Hz); ^{13}C NMR δ 258.28 (C=O, J_{C-P} = 13.1 Hz), 206.61 (C≡O, J_{C-P} = 20.1 Hz), 202.65 (C≡O), 202.45 (C≡O), 88.39 (C$_5$H$_5$) and 88.17 (C$_5$H$_5$), 26.92 (CH$_2$, J_{C-H} = 132.0, $J_{C-H'}$ = 137.0 Hz), 21.11 (PMe$_3$, J_{C-P} = 32.9 Hz); IR (hexane) 2022 (s), 1968 (s), 1928 (s), 1568 cm^{-1} (m, br). Anal. Calcd (found): C, 40.45 (40.18); H, 3.90 (3.93).

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[12] Y. C. Lin and S. S. Wreford, unpublished results.

[13] The complexes [CpFe(CO)$_2$]$_2$[μ-(CH$_2$)$_n$] (n = 3, 4, and 5) have been previously prepared: (a) King, R. B. *Inorg. Chem.* **1963**, *2*, 531. (b) King, R. B.; Braitsch, D. M., *J. Organomet. Chem.* **1973**, *54*, 9. (c) Cooke, M.; Forrow, N. J.; Knox, S. A. R. *Ibid.* **1981**, *222*, C21.

[14] Other C$_2$H$_4$-bridged complexes are known and decompose by elimination of ethylene: Beck, W.; Olgemöller, B. *J. Organomet. Chem.* **1977**, *127*, C45.

Preparation and Characterization of Novel μ_3-N$_2$ Mixed Metal Complexes[1]

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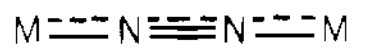
Extensive studies on the reactions of coordinated dinitrogen have shed some light on the mechanism for its reduction into ammonia and hydrazine under mild conditions.[2] Previously we reported that ligating dinitrogen in molybdenum and tungsten complexes *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**1**, M = Mo or W) are reduced stepwise into nitrogen hydrides via diazenido (M=N=N—H) and hydrazido(2−) (M=N—NH$_2$) complexes, which are formed by the electrophilic attack of proton on the terminal nitrogen.[3] These findings have led us to expect that treatment of dinitrogen complexes with some kinds of Lewis acids instead of a proton may form μ_2- or μ_3-N$_2$ complexes (metallodiazenido or hydrazido(2−) complexes) in which two different metals are bonded to each nitrogen atom.

Several types of polynuclear μ-N$_2$ complexes are already known. Many μ-N$_2$ complexes with a linear M-N-N-M moiety (type I) such as [(NH$_3$)$_5$RuN$_2$Ru(NH$_3$)$_5$][(BF$_4$)$_4$],[4] {MoCl$_4$[ReCl(PMe$_2$Ph)$_4$(N$_2$)]$_2$},[5] and [TaCl(C$_2$H$_4$)(PMe$_3$)$_3$]$_2$(μ-N$_2$)[6] have been prepared, the latter of which reacts with acetone to give dimethylketazine. An end-on bonded and sideways bonded dinitrogen ligand of type II has been found in a triply bridged dinitrogen complex of titanium with (μ_3-N$_2$)[(η^5:η^5-C$_{10}$H$_8$)(η-C$_5$H$_5$)$_2$Ti$_2$][(η^1:η^5-C$_5$H$_4$)(η-C$_5$H$_5$)$_3$Ti$_2$] unit.[7] Novel polynuclear dinitrogen complexes of nickel such as [(PhLi)$_6$Ni$_2$(N$_2$)(Et$_2$O)$_2$]$_2$[8]



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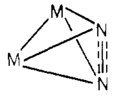
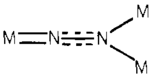
II



III



IV

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[1] Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 18. For part 17 of this series, see: Hidai, M.; Yokotake, I.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1982**, 453–454.

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