should exhibit AB coupling and both two-bond and four-bond coupling to the magnetically nonequivalent phosphorus nuclei.

In a formal sense, as suggested in Scheme I, 2 may be regarded as the product of a reaction between (L-L) and $CH_3Mn(CO)_5$ in which one molecule of methane and two molecules of carbon monoxide are eliminated per mole of reagents. Alternatively, the eliminated species might be acetaldehyde and carbon monoxide or even ketene and dihydrogen. At this time, no substance other than 2 has been identified as a product of this reaction. Although the initial steps in the overall process leading to 2 probably include well understood reactions such as methyl migration and decarbonylation, no unique mechanism for subsequent steps (e.g. agostic and/or four-center interactions)[12] can be advanced at this time. Nevertheless, the overall process most likely involves (1) loss of a methyl or acetyl group attached to manganese and (2) metalation of a methyl group on silicon. Precedence has been established for each of these two processes, as shown in the following paragraphs. However, to our knowledge, there has been no previously reported observation of these two processes occurring simultaneously, or in a stepwise manner, at manganese.

Two reports of reductive elimination of an alkane in which the alkyl moiety resides originally on manganese may be cited. Kaesz and his co-workers observed elimination of methane in the reactions between $CH_3Mn(CO)_5$ and bis(cyclopentadienyl)tungsten, -molybdenum, and rhenium hydrides.[13] Later, Halpern and his co-workers showed a similar elimination of substituted toluenes or phenylacetaldehydes from selected benzylmanganese carbonyl complexes upon reaction with related hydridomanganese carbonyl complexes.[14] The latter study showed very clearly that at least four different modes of reductive elimination are possible in this chemistry.

The activation of C–H bonds in tetramethylsilane by alkylmetal complexes was first reported by Watson.[15] Specifically, $(\eta^5\text{-}C_5Me_5)_2Lu\text{–}CH_3$ was observed to react with tetramethylsilane at 40 °C in cyclohexane with elimination of methane and formation of the metalated product $(\eta^5\text{-}C_5Me_5)_2Lu\text{–}CH_2SiMe_3$. Similar activation of tetramethylsilane by thorium derivatives was demonstrated by Marks and his co-workers.[16]

The formation of 2 under our reaction conditions appears to be an example of a facile intramolecular process that incorporates the two well-documented types of intermolecular reactions described above. The ease with which this intramolecular reaction occurs at manganese is reasonable inasmuch as C–H bond activation has been demonstrated to occur readily whenever intramolecular reaction is possible.[17]

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Registry No. 2, 114762-77-5; $(C_6H_5)_2PCH_2Si(CH_3)_2SiCH_2P(C_6H_5)_2$, 59557-18-5; $CH_3Mn(CO)_5$, 13601-24-6.

Supplementary Material Available: ORTEP drawing and a 3D stereoplot and tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom and atomic coordinates (7 pages); listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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A Convenient Route to an Uncommon Class of Polymeric and Binuclear Ruthenium(I) Complexes Containing Diphosphine and Dithioether Ligands

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Summary: Reaction of either the carboxylate-bridged dimers $[Ru(CO)_2(\mu\text{-}O_2CR)(NCMe)]_2$ or the polymeric dimers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]_n$ (R = Me, Et) with 1 equiv (per dimer unit) of the bidentate groups L_2 ($L_2 = R'_2PCH_2PR'_2$, R′ = Ph (DPPM), Me (DMPM); $L_2 = R'SCH_2SR'$, R′ = Ph, Me) yields the unusual Ru(I) polymers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(L_2)]_n$, in which two metals are bridged by two carboxylate groups and these binuclear units are linked by diphosphine or dithioether ligands. Reaction with 2 equiv of the diphosphine $Ph_2PCH_2PPh_2$ in THF yields the neutral disubstituted dimer $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-}DPPM)_2]$, whereas with DPPM or $Ph_2P(CH_2)_2PPh_2$ (DPPE) in alcohols two types of cationic compounds of formula $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(L_2)_2]^+$ (L_2 = DPPM, DPPE) are obtained. The X-ray structures of both cationic species have been determined and show that one has the Ru(I) centers bridged by two DPPM and one acetate ligand, whereas the other has two bridging carbonyls and one bridging acetate group, with one DPPE chelating each metal.

The recent interest in binuclear complexes, particularly of the group 8 metals, has been brought about, to a large degree by the anticipation that such complexes may display metal–metal cooperativity effects in substrate activation and catalysis.[1-5] One major class of binuclear

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complexes has utilized diphosphine ligands such as bis(diphenylphosphino)methane (DPPM)[6] and bis(dimethylphosphino)methane (DMPM)[7] to hold the metals in close proximity while some degree of flexibility is still allowed within the complex. To date, the vast majority of these DPPM- and DMPM-bridged complexes has involved the platinum group metals, Rh, Ir, Pd, and Pt, with surprisingly little having been reported for ruthenium, in spite of suggestions[8] that binuclear ruthenium(I) complexes may be involved as intermediates in homogeneously catalyzed reactions. A few related complexes involving the diphosphazane bridging group[9] and some mixed Ru/Rh[10a,b] and Ru/Mo[10c] DPPM-bridged complexes have been studied; however, the chemistry of homobinuclear, diphosphine-bridged complexes of Ru(I) remains largely unexplored.[11] It is also worthy of note that irrespective of bridging group, there are very few binuclear complexes of ruthenium(I),[11-14] although a high-yield route to one class of such complexes has recently been reported.[15] The paucity of diphosphine-bridged diruthenium(I) complexes appears to be due to the lack of suitable precursors, with the majority of species having been obtained in low yields by the degradation of $Ru_3(CO)_{12}$ and other substituted triruthenium clusters.[16]

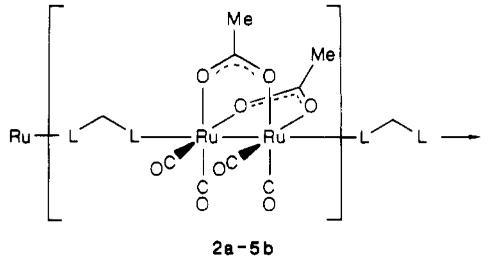
In this paper we report a convenient, high-yield route to a class of mono- and disubstituted diphosphine and dithioether complexes of Ru(I), starting from either the polymeric dimer $[Ru_2(CO)_4(O_2CR)_2]_n$ or the related acetonitrile adduct $[Ru(CO)_2(O_2CR)(NCMe)]_2$ (**1**).[17]

Reaction of the carboxylate-bridged dimers $[Ru(CO)_2(\mu\text{-}O_2CR)(NCMe)]_2$ (R = Me (**1a**), Et (**1b**)) with 1 equiv of the diphosphine (DPPM or DMPM) or dithioether ($R'SCH_2SR'$, R′ = Me, Ph) ligands yields the yellow compounds $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(L_2)]$,[18] in essentially quantitative yields, according to eq 1. On the basis of the data

$$[Ru(CO)_4(\mu\text{-}O_2CR)(NCMe)]_2 + L_2 \xrightarrow{THF} [Ru_2(CO)_2(\mu\text{-}O_2CR)_2(L_2)] + 2MeCN \quad (1)$$

$L_2 = Ph_2PCH_2PPh_2$, R = Me (**2a**), Et (**2b**);
$L_2 = Me_2PCH_2PMe_2$, R = Me (**3a**), Et (**3b**);
$L_2 = PhSCH_2SPh$, R = Me (**4a**), Et (**4b**);
$L_2 = MeSCH_2SMe$, R = Me (**5a**), Et (**5b**)

presented below, we propose the structure shown in which the two ruthenium atoms are bridged by two carboxylate groups and the dinuclear units are linked by diphosphine or dithioether ligands to form chains.



2a-5b

L⌒L = Ph₂PCH₂PPh₂, Me₂PCH₂PMe₂, PhSCH₂SPh, MeSCH₂SMe

1. The IR spectra of these compounds display four sharp bands in the terminal carbonyl region in addition to a strong band between 1565 and 1575 cm^{-1}, consistent with a bridging carboxylate stretch.[19] This corresponds with the spectra previously observed for cisoid bis(μ-acetato)dimetal tetracarbonyls[20] having the carbonyl groups in a C_{2v} sawhorse arrangement. Such a core structure thus eliminates the possibility of a Ru–Ru dimer bridged by the diphosphine or dithioether ligands.

2. The known[12] DPPM-bridged dimer $[Ru_2(CO)_4(\mu\text{-}I)_2(\mu\text{-}DPPM)]$,[21] formed by us from **2a** and LiI, differs

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(18) Anal. Calcd for $Ru_2(CO)_4(O_2CMe)_2$(DPPM): C, 48.52; H, 3.43. Found: C, 48.26; H, 3.46. IR (Nujol, cm^{-1}): ν(CO) 2023 vs, 1978 s, 1952 s, 1911 w; $\nu(CO_2)$ 1577 s. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, −40 °C): δ 14.9 (s). Anal. Calcd for $Ru_2(CO)_4(O_2CMe)_2$(DMPM): C, 27.46, H, 3.52. Found: C, 27.25; H, 3.46. IR (Nujol, cm^{-1}): ν(CO) 2009 s, 1965 s, 1945 s, 1934 w; $\nu(CO_2)$ 1575 s. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, −40 °C): δ −7.55 (s). Anal. Calcd for $Ru_2(CO)_4(CH_3CH_2CO_2)_2$(DPPM): C, 49.76; H, 3.70. Found: C, 50.09; H, 4.16. IR (Nujol, cm^{-1}): ν(CO) 2019 s, 1978 s, 1947 s, 1920 w; $\nu(CO_2)$ 1568 (s). IR (THF, cm^{-1}): ν(CO) 2022 s, 1978 s, 1950 s, 1920 w; $\nu(CO_2)$ 1565 s. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, −40 °C): δ 14.97 (s). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.9 (t, CH_3), 2.14 (q, CH_2CH_3), 4.03 (br s, PCH_2P), 7.12 (m), 7.14 (m), 7.36 (br s, *Ph*). Anal. Calcd for $Ru_2(CO)_4(O_2CEt)_2$(DMPM): C, 31.04; H, 4.02. Found: C, 30.71; H, 4.19. IR (Nujol, cm^{-1}): ν(CO) 2011 s, 1966 s, 1942 s, 1911 w; $\nu(CO_2)$ 1569 s. IR (THF, cm^{-1}): ν(CO) 2016 s, 1966 s, 1950 s, 1940 s, 1912 w; $\nu(CO_2)$ 1569 s. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 20 °C): δ −4.02 s. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.00 (t, CH_3), 1.64 (s, P*Me*), 2.22 (q, CH_2CH_3), 2.50 (br s, PCH_2P). Anal. Calcd for $Ru_2(CO)_4(O_2CMe)_2(PhSCH_2SPh)$: C, 37.95; H, 2.71. Found: C, 37.94; H, 3.34. IR (Nujol, cm^{-1}): ν(CO) 2029 s, 1984 s, 1957 s, 1924 w; $\nu(CO_2)$ 1569 s. IR (THF, cm^{-1}): ν(CO) 2036 s, 1985 s, 1952 s, 1949 s, 1922 w; $\nu(CO_2)$ 1571 s. Insufficient solubility for satisfactory ^1H NMR spectrum. Anal. Calcd for $Ru_2(CO)_4(O_2CMe)_2(MeSCH_2SMe)$: C, 24.44; H, 2.59; S, 11.85. Found: C, 24.44; H, 2.59; S, 12.43. IR(Nujol, cm^{-1}): ν(CO) 2022 s, 1979 s, 1963 s, 1943 s, 1924 w; $\nu(CO_2)$ 1574 s. IR (THF, cm^{-1}): ν(CO) 2030 s, 1988 s, 1951 ssh, 1949 s, 1920 w; $\nu(CO_2)$ 1572 s. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ 4.09 (s, SCH_2S), 2.46 (s, CH_3S), 1.95 (s, CH_3CO_2). Anal. Calcd for $Ru_2(CO)_4(O_2CEt)_2(PhSCH_2SPh)$: C, 39.88; H, 3.18; S, 9.25. Found: C, 39.46; H, 3.34; S, 9.00. IR (Nujol, cm^{-1}): ν(CO) 2028 s, 1982 m, 1951 s, 1922 w; $\nu(CO_2)$ 1571 s. IR (THF, cm^{-1}): ν(CO) 2032 s, 1986 s, 1964 ssh, 1950 s, 1921 w; $\nu(CO_2)$ 1571 s. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.03 (t, CH_2CH_3), 2.22 (q, CH_2CH_3), 4.90 (br s, SCH_2S), 7.6 (s, Ph), 7.4 (s, Ph). Anal. Calcd for $Ru_2(CO)_4(O_2CEt)_2(MeSCH_2SMe)$: C, 27.46; H, 3.17, S, 9.00. Found: C, 27.35; H, 3.61; S, 8.62. IR(Nujol, cm^{-1}): ν(CO) 2026 s, 1975 s, 1963 s, 1927 w, 1915 wsh; $\nu(CO_2)$ 1569 s. Insufficiently soluble for ^1H NMR spectrum.

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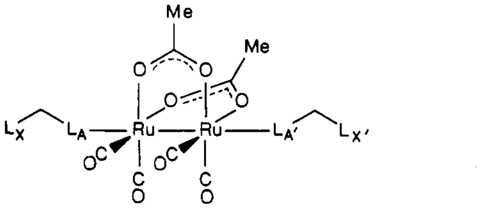
markedly in the carbonyl stretching region of the IR from those of **2a**–**5b**.

3. Complexes **2a**–**5b** have very limited solubilities which mirror the insoluble nature of the polymer $[Ru_2(CO)_4(O_2CR)_2]_n$ and are in sharp contrast to the high degree of solubility exhibited by the dimers $[Ru_2(CO)_4(O_2CR)_2(L)_2]$ (L = MeCN, PPh_3, $P(p\text{-}C_6H_4F)_3$[17]).

4. The structure of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(MeSCH_2SMe)]_n$ (**5a**) has been determined by X-ray techniques[22] and has been shown to have the polymeric structure proposed.

Treatment of the acetonitrile dimer **1a** with 2 molar equiv per dimer of DPPM in refluxing THF gave a quantitative yield of the yellow crystalline complex $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-DPPM})_2]$ (**6**). The similarity between the IR spectrum[23] in the carbonyl and carboxylate vibration region of **6** and those of **2a**–**5b** suggests an identical core structure for these compounds. The $^{31}P\{^1H\}$ NMR spectrum of **6** appears as two sets of multiplets[23] at δ 14.9 and −26.3 consistent with an AA′XX′ spin system and corresponds closely with the $^{31}P\{^1H\}$ NMR resonances observed for $[Os_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-DPPM})_2]$ which has been structurally characterized.[24] Consequently the following structure, having the DPPM ligands coordinated in a η^1 fashion trans to the metal–metal bond, is proposed.



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L⌒L = $Ph_2PCH_2PPh_2$

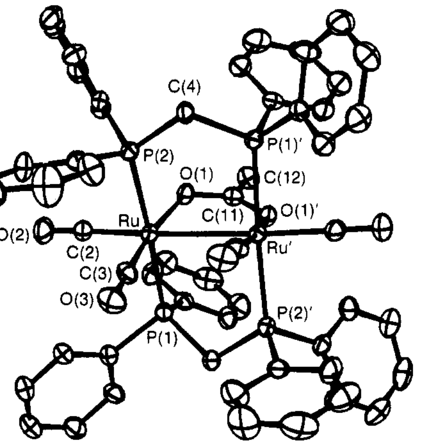

Figure 1. A perspective view of the $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(DPPM)_2]^+$ cation showing the numbering scheme. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Ru–Ru = 2.841 (1), Ru–C(2) = 1.914 (6), Ru–C(3) = 1.825 (8), Ru–O(1) = 2.129 (5), Ru–P(1) = 2.372 (2), Ru–P(2) = 2.374 (2), Ru′–Ru–C(2) = 173.0 (1), Ru′–Ru–C(3) = 90.4 (1), Ru′–Ru–O(1) = 80.9 (1), Ru′–Ru–P(1) = 91.0 (1), Ru′–Ru–P(2) = 92.2 (1).

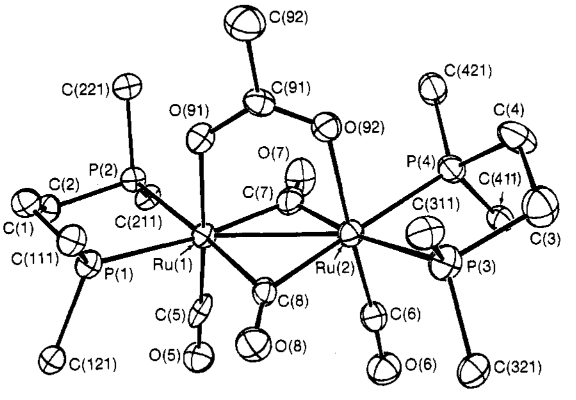

Figure 2. A perspective view of the $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(DPPE)_2]^+$ cation showing the numbering scheme. Thermal ellipsoids at the 30% level are shown. Only the first carbon of each phenyl ring is shown, and hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)–Ru(2) = 2.750 (1), Ru(1)–C(5) = 1.79 (1), Ru(1)–C(7) = 2.09 (1), Ru(1)–C(8) = 2.09 (1), Ru(1)–O(91) = 2.111 (7), Ru(1)–P(1) = 2.382 (3), Ru(1)–P(2) = 2.399 (3), Ru(2)–C(6) = 1.83 (1), Ru(2)–C(7) = 2.09 (1), Ru(2)–C(8) = 2.06 (1), Ru(2)–O(92) = 2.122 (7), Ru(2)–P(3) = 2.409 (3), Ru(2)–P(4) = 2.395 (3), Ru(1)–C(7)–Ru(2) = 82.3 (5), Ru(1)–C(8)–Ru(2) = 83.0 (4), Ru(2)–Ru(1)–O(91) = 82.3 (2), Ru(2)–Ru(1)–C(5) = 101.3 (3), Ru(1)–Ru(2)–O(92) = 83.2 (2), Ru(1)–Ru(2)–C(6) = 99.0 (3).

In refluxing alcohols the cationic disubstituted species, having the formulation $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(L_2)_2]^+$, preferentially form from reactions of the polymer with 2 molar equiv per dimer of the ligands L_2 = DPPM, DMPM, DPPE (bis(diphenylphosphino)ethane), and DIARS (bis(diphenylarsino)ethane). The compound $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(DPPM)_2]^+$ can also be prepared by the addition of 1 equiv of DPPM to **2a** in refluxing EtOH, a route which suggests the possibility of preparing Ru(I) dimers bridged by three different bridging groups (acetate plus two of either DPPM, DMPM, $PhSCH_2SPh$, or $MeSCH_2SMe$). In addition this complex can be prepared from **6** by converting it to the cationic form in refluxing ethanol. Here only the products formed with DPPM and DPPE will be considered because of their contrasting substitution patterns. Addition of NH_4PF_6 to the reaction solution of the acetate-bridged polymer and 2 equiv of L_2 gave a high yield of the yellow and purple complexes $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(L_2)_2]PF_6$ (L_2 = DPPM (**7a**), DPPE (**7b**), respectively). The IR spectra[25,26] of these species differ consid-

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(21) Anal. Calcd for $Ru_2(CO)_4(I)_2(DPPM)$: C, 36.5; H, 2.3; I, 26.6. Found: C, 36.1; H, 2.3; I, 24.4. IR (Nujol, cm^{-1}): ν(CO) 2023 s, 2002 s, 1965 s, 1950 w. $^{31}P\{^1H\}$ NMR (36.4 MHz, 20 °C): δ 17.3 (s). ^1H NMR ($CDCl_3$, 20 °C): δ 4.90 (d, PCH_2P, $J_{PH} \approx 10$ Hz), 7.31 (m, P*Ph*).

(22) Preliminary crystal data for $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)_2(MeSCH_2SMe)]_n$: triclinic, space group $P\bar{1}$; $a = 15.838$ (2) Å, $b = 17.562$ (2) Å, $c = 8.238$ (2) Å; $\alpha = 102.55$ (1)°, $\beta = 101.87$ (1)°, $\gamma = 68.17$ (1)°; $V = 2056.3$ Å^3; $Z = 2$ (per tetranuclear unit); $D_{calcd} = 1.75$ g cm^{-3}; λ(Mo Kα) = 0.71073 Å; yellow crystal. Cell and intensity data were measured on an Enraf-Nonius CAD4F diffractometer with graphite-monochromated Mo Kα radiation up to $\theta = 25.0°$. Data were corrected for Lorentz and polarization effects but not yet for absorption. Hydrogen atoms are not yet included. The structure was solved by using MULTAN and has refined, using isotropic thermal parameters, to $R = 0.079$ and $R_w = 0.110$, for 185 variables and 3515 unique observations. The polymer chains are comprised of the two independent "$Ru_2(CO)_4(\mu\text{-}O_2CCH_3)_2$" moieties linked together by both ends of the $MeSCH_2SMe$ groups. Each of these dimer units has a Ru–Ru bonded (2.678 (2), 2.685 (2) Å) "sawhorse" type arrangement in which the mutually cis carbonyl groups on each metal are trans to the bridging acetate groups. The orientations of these dimer units alternate along the polymer chain having the acetates from one unit on the same side of the chain as the carbonyls from the adjacent units. The $MeSCH_2SMe$ groups link the dimeric units through the axial positions opposite the Ru–Ru bonds (Ru–S distances range from 2.485 (4) Å to 2.508 (4) Å). Parameters involving the acetate and carbonyl groups are normal.

(23) Anal. Calcd for $[Ru_2(CO)_4(\mu\text{-}O_2Me)_2(\eta^1\text{-DPPM})_2]$: C, 58.0; H, 4.17. Found: C, 58.13; H, 4.64. mp: 95 °C. IR (Nujol, cm^{-1}): ν(CO) 2012 vs, 1972 s, 1940 vs, 1900 sh; ν(CO_2) 1573. IR (CH_2Cl_2, cm^{-1}). ν(CO) 2022 vs, 1976 s, 1947 vs; ν(CO_2) 1573 s, 1436 s. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 30 °C); AA′XX′, δ 14.87, −26.32 (^2J(PCP) = 63 Hz, ^3J(PRuRuP) = 115 Hz). ^1H NMR (300 MHz, $CDCl_3$, 30 °C): δ 1.58 (s, *Me*), 3.30 (d, CH_2), 7.29–7.14 (m, *Ph*), 7.52 (m, *Ph*).

(24) Albers, M. O.; Singleton, E.; Steyn, M. M. de V., unpublished results.

erably, with **7a** containing only terminal carbonyls and **7b** containing both terminal and bridging carbonyl stretching vibrations. The $^{31}P\{^1H\}$ NMR spectra show singlets at δ 30.4 for **7a** and at δ 42.9 for **7b**, in the regions typical for bridging DPPM[27] and chelated DPPE,[28] respectively. Compounds **7a** and **7b** have been elucidated by X-ray structural determinations.[29,30]

For $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)(DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$, an ORTEP diagram of the cation is shown in Figure 1. Both metals have almost undistorted octahedral geometries and are bridged by the two DPPM groups in a mutually trans arrangement and by the acetate group. The Ru–Ru separation of 2.841 (1) Å is consistent with a single bond, as expected for a Ru(I)/Ru(I) dimer, and this relatively short separation results in a slight twist of the substituents on each metal from an exactly eclipsed conformation, yielding torsion angles about the Ru–Ru bond of between 17.3 (2)° and 20.6 (4)°. There is a pronounced difference in the Ru–C distances for the axial (1.914 (6) Å) and equatorial (1.825 (8) Å) carbonyl ligands, possibly reflecting either the π-donor ability of the acetate group opposite the equatorial CO's or the large trans influence of the metal–metal bond.[31] Structurally this species resembles $[Ru_2(\mu\text{-}OB(F)OH)(CO)_4(i\text{-}PrO)_2PN(Et)P(O\text{-}i\text{-}Pr)_2)_2][BF_4]$[9a] which has a comparable Ru–Ru distance of 2.814 (1) Å.

An ORTEP representation of the complex cation of $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CMe)(DPPE)_2][PF_6]$ (**7b**) is shown in Figure 2. The Ru–Ru separation in this dimer (2.751 (1) Å) is somewhat shorter than in **7a** but is still consistent with a normal single bond. If we ignore this bond, the complex can be described as a bioctahedron sharing an edge at the bridging carbonyl groups. Angles about the Ru atoms range from 82.9 (2)° to 96.7 (4)°, indicating only slight distortions from idealized octahedral geometries. The small bite of the bridging acetate group causes a slight tilt, by 21.5 (2)°, of the two Ru equatorial planes and puckering about the axis containing the bridging carbonyl ligands. All other parameters within the complex are as expected.

Formation of a diphosphine-bridged species with DPPM but a chelating-diphosphine species with DPPE is not unexpected on the basis of the normal tendencies of these groups; however, it does result in two interesting variations in these unusual types of diphosphine-containing diruthenium(I) complexes. The convenient routes to these complexes, reported herein, significantly extend the known types of diruthenium(I) complexes, which until now have been rather scarce. It is anticipated that with these diphosphine- and dithioether-bridged species the chemistry associated with adjacent Ru(I) centers can be probed.

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Registry No. **1a**, 24846-20-6; **1b**, 96317-57-6; **2a**, 108294-67-3; **2b**, 114550-94-6; **3a**, 114550-93-5; **3b**, 114550-95-7; **4a**, 114550-96-8; **4b**, 114550-98-0; **5a**, 114550-97-9; **5b**, 114550-99-1; **6**, 114551-05-2; **7a**·2(CH$_3$)$_2$CO, 114551-02-9; **7b**, 114551-04-1; $[Ru_2(CO)_4(\mu\text{-}I)_2(\mu\text{-}DPPM)]$, 103538-15-4; $[Ru_2(CO)_4(O_2CCH_3)_2]_n$, 89689-03-2; Ru, 7440-18-8.

Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, and listings of bond lengths and angles for compounds **7a** and **7b** (18 pages); listings of structure factor amplitudes for **7a** and **7b** (57 pages). Ordering information is given on any current masthead page.

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(25) Anal. Calcd for $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(\mu\text{-}DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$: C, 53.07; H, 4.24. Found: C, 52.33; H, 4.29. mp: 128 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2023 s, 2006 s, 1963 m, 1934 w; $\nu((Me)_2CO)$ 1713 m; $\nu(CO_2)$ 1541 s; $\nu(PF_6)$ 847 m. $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6, 30 °C): δ 30.36 (s). ^1H NMR (500 MHz, acetone-d_6 30 °C): δ 0.76 (s, *Me*), 2.08 (s, *Me*), 4.43 (dt, CH_2, J(HH) = 15.2, J(PCH) = 5.5 Hz), 4.93 (dt, CH_2, J(HH) = 15.2, J(PCH) = 4.2 Hz), 7.41 (m, *Ph*), 7.47 (m, *Ph*), 7.56 (m, *Ph*), 7.64 (m, *Ph*).

(26) Anal. Calcd for $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CMe)(DPPE_2)][PF_6]$: C, 52.98; H, 3.19. Found: C, 52.95; H, 3.88. mp: 225 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2004 s, 1944 sh, 1750 m; $\nu(CO_2)$ 1549; $\nu(PF_6)$ 847 s. $^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 30 °C): δ 42.85 s. ^1H NMR (500 MHz, acetone-d_6, 30 °C): δ 0.90 (s, *Me*), 3.00 (br s, C_2H_4), 3.14 (br s, C_2H_4), 7.33 (m, *Ph*), 7.50 (m, *Ph*), 7.57 (m, *Ph*), 7.82 (m, *Ph*).

(27) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*.

(28) Pomeroy, R. K.; Wijesekera, K. S. *Can. J. Chem.* **1980**, *58*, 206.

(29) Crystal data for $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)(\mu\text{-}DPPM)_2][PF_6]\cdot 2(CH_3)_2CO$: $C_{62}H_{59}F_6O_8P_5Ru_2$; M_r 1403.14; monoclinic, space group $C2$; a = 19.354 (3) Å, b = 15.126 (2) Å, c = 10.780 (2) Å; β = 91.68 (1)°; V = 3154.5 Å^3; Z = 2; D_{calcd} = 1.48 g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; μ = 0.594 mm^{-1}; $F(000)$ = 1423.98. A yellow crystal with dimensions 0.37 × 0.33 × 0.20 mm was used. Cell parameters and intensity data were measured on an Enraf-Nonius CAD4F diffractometer with graphite-monochromated Mo Kα radiation in the range $3 < \theta < 30°$. Data were corrected for Lorentz and polarization effects and for absorption (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351). The structure was solved by Patterson and difference electron density synthesis methods using the ShelX program (Sheldrick, G. M. *Computing in Crystallography*; Delft University: Delft, 1978) and was refined to a current R_w of 0.041 for 350 parameters and 4338 reflections with $F_o \le 5\sigma(F_o)$ and a weighting scheme of $w = 1.7506/\sigma^2(F_o)$. The molecule resides on a crystallographic twofold rotation axis with acetate carbon atoms and the counterion phosphorous atom on special positions. Phenyl hydrogens were idealized and not refined, and acetate hydrogens were omitted since these could not be accommodated by the twofold symmetry. The y coordinate of ruthenium was fixed to define the origin. Non-hydrogen atoms, except for fluorine atoms and solvate carbon and oxygen atoms, were refined anisotropically; others were refined isotropically.

(30) Crystal data for $[Ru_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}O_2CCH_3)(DPPE)_2][PF_6]$: $C_{58}H_{51}F_6O_6P_5Ru_2$; M_r 1315.0; monoclinic, space group $P2_1/c$; a = 16.141 (5) Å, b = 13.904 (5) Å, c = 25.189 (4) Å; β = 94.11 (3)°; V = 5638.36 Å^3; Z = 4; D_{calcd} = 1.55 g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; μ = 0.659 mm^{-1}; $F(000)$ = 2655.96. A crystal with dimensions 0.40 × 0.15 × 0.08 mm was used. Data collection (to θ = 23°), data reduction, and structure solution were performed as described in ref 24. The structure was refined as a blocked matrix to a current R_w of 0.053 for 726 parameters and 5120 reflections with $F_o \le 2\sigma(F_o)$ and a weighting scheme of $w = 1.2565/\sigma^2(F_o)$. Hydrogen atoms were idealized and not refined. Non-hydrogen atoms were refined with anisotropic and hydrogen atoms were assigned isotropic thermal parameters.

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Generation of a 1-Ferracyclobutene from Thermal and Photolytic Induced Rearrangement of α-Ethoxycyclopropyl σ Complexes of Iron

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Summary: A 1-ferracyclobutene (**11**) has been isolated from photolysis of the (η^5-cyclopentadienyl)dicarbonyliron complex of 1-ethoxycyclopropane (**9a**). This same material is apparently also formed from thermolysis of the Ph_3P-substituted σ-complex **9b**. The chemistry of this highly unstable metallacycle includes migratory CO insertion to form the ferracyclopentenones **12a** and **12b** (in the presence of added CO and Ph_3P, respectively), ring contraction to the 16-electron intermediate **10**, and ring opening (tentative) to the terminally substituted π-allyl complex **14**. The 16-electron intermediate **10** also slowly ring opens to the centrally substituted π-allyl complex **13**.

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