channel selectivity produces acetone, causing the amount of acetone to exceed the amount of aldehyde for long reaction times. Consistent with this mechanism, the concentration of acetone is not found to exceed that of acetaldehyde until the concentration of $PtCl_6^{2-}$ drops to a very low concentration (see Figure 1).

In order to test this overall mechanism, the photochemistry of $PtCl_6^{2-}$ with *tert*-butyl alcohol was observed. Analysis of the photolysis products indicated acetone as the organic product and $PtCl_4^{2-}$ as the inorganic product. No metal formation was observed after prolonged photolysis. Since acetone can only be derived in this case by the generation of an oxygen-based *tert*-butoxy radical, followed by methyl radical loss, the one-electron oxidation of *tert*-butyl alcohol and concomitant formation of a Pt(III) intermediate are confirmed. Further, the lack of Pt metal and preponderance of Pt(II) serve to substantiate the presence of reaction 2 during the photolysis of $PtCl_6^{2-}$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $PtCl_6^{2-}$, 16871-54-8; $PtCl_4^{2-}$, 13965-91-8; Pt, 7440-06-4; ethanol, 64-17-5; 2-propanol, 67-63-0; acetaldehyde, 75-07-0; acetone, 67-64-1; *tert*-butyl alcohol, 75-65-0.

Contribution from the Department of Chemistry,
Queen's University, Kingston, Canada K7L 3N6

A New Form of Ruthenium Tetracarbonyl

W. Ross Hastings and Michael C. Baird*

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At present there are known only three binary carbonyl compounds of ruthenium, $Ru(CO)_5$ (I), $Ru_2(CO)_9$ (II), and $Ru_3(CO)_{12}$[1] (III). Of these, III is the thermodynamically most stable and is formed spontaneously when either of the others is allowed to stand in the absence of a partial pressure of CO. However, I can be readily prepared either thermally or photochemically from reactions of III with CO, while II can be formed by low-temperature photolysis of I.[1]

While extending an investigation[2] into the utilization of ruthenium carbonyls as precursors for catalysts for CO and CO_2 hydrogenation, we have had cause to prepare I photochemically from the reaction of CO with III.[3] Interestingly, we have found that photolysis of *concentrated* solutions of III (p_{CO} = 1 atm) in tetrahydrofuran or hydrocarbon solvents leads to formation, in addition to I, of an insoluble, purple-red material that appears to be an oligomeric form of $Ru(CO)_4$ (IV). We describe below the physical and chemical properties of IV that lead us to this conclusion.[4]

Experimental Section

$Ru_3(CO)_{12}$ (III) was prepared from $RuCl_3 \cdot 3H_2O$ by the method of Johnson and Lewis,[6] while photochemical reactions were performed with quartz apparatus and a Hanovia lamp positioned about 1 cm from the reaction mixture. Solvents were dried and degassed prior to use, and all operations were carried out under an atmosphere of carbon monoxide or nitrogen. IR spectra were run on a Bruker IFS 85 FTIR spectrometer, and gas chromatography experiments were carried out with an HP 5880A instrument equipped with an *n*-octane Porasil-C column. X-ray powder diffraction patterns were obtained by utilizing a CSS/Stoe STADI 2/PL two-circle diffractometer. The data, along with comparable data for III, are being submitted to the JCPDS International Centre for Diffraction Data, Swarthmore, PA 19081. Carbon and hydrogen analyses were performed by the Canadian Microanalytical Service, Ltd., ruthenium analyses (neutron activation) by the Analytical Services Unit at Queen's University utilizing the SLOWPOKE-II facility at the Royal Military College of Canada.

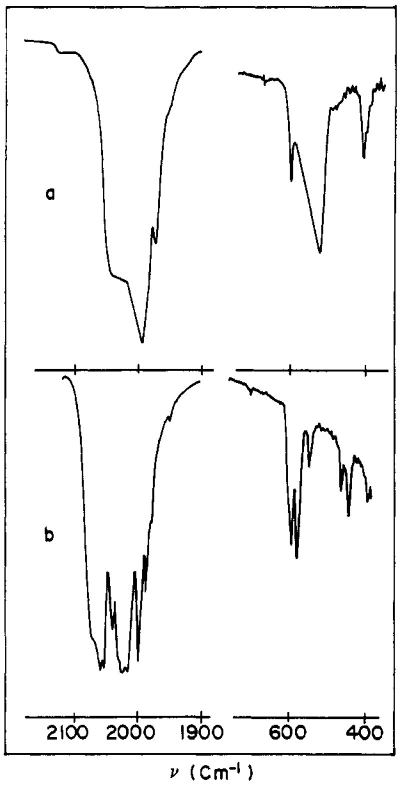

Figure 1. IR spectra (KBr disks) of $[Ru(CO)_4]_n$ (a) and $Ru_3(CO)_{12}$ (b).

Preparation of $[Ru(CO)_4]_n$ (IV). A solution of 1.00 g (1.6 mmol) of III in 200 mL of THF at about 20 °C was photolyzed for 12 h under an atmosphere of CO. A first crop of 0.3 g (30% yield) of IV was scraped from the inner cooling jacket of the photochemical apparatus, and the decanted solution was rephotolyzed to give a further 0.2 g. This procedure could be repeated to give total yields of at least 80%. The product was washed by prolonged suspension in THF to remove residual III and was dried in vacuo. It is a microcrystalline solid, nonvolatile and highly insoluble in common organic solvents. Anal. Calcd for C_4O_4Ru: C, 22.54; H, 0; Ru, 47.4. found: C, 22.04; H, <0.1; Ru, 46.9. The IR spectrum in the regions 400–700 and 1900–2150 cm^{-1} (KBr disk) is shown in Figure 1, where it is compared with an IR spectrum of $Ru_3(CO)_{12}$ run under similar conditions.

In constrast to the above, photolysis of dilute solutions of III (less than 0.05 g in 200 mL of solvent) results in the formation only of I.

Reaction of IV with CO. A suspension of 0.1 g of IV in petroleum ether (bp 40–60 °C) in a glass-lined 300-mL Parr stirring minireactor was treated with about 50 atm of CO at 80 °C for 16 h. After cooling and opening of the reactor under nitrogen, the solution was found to contain (IR) only I (ν(CO) = 2037 (s), 2002 (vs) cm^{-1}) and III (ν(CO) = 2061 (vs), 2032 (s), 2012 (m) cm^{-1}).

Reaction of IV with H_2. Similar reaction with hydrogen resulted in the formation only of $H_4Ru_4(CO)_{12}$, identified initially by comparison of its IR spectrum (ν(CO) = 2081 (s), 2067 (vs), 2030 (m), 2024 (s), 2008 (w) cm^{-1}) with that of an authentic sample.[7] A $CDCl_3$ solution of the compound exhibited a hydride resonance at δ – 17.8 ppm, in agreement with the literature.

Reactions of IV with Halogens. A mixture of 0.025 g (0.12 mmol of Ru) of IV and 0.03 g (0.12 mmol) of iodine in 15 mL of methylene chloride was stirred for 48 h at room temperature under nitrogen. The suspension of IV gradually disappeared, the solution turning yellow. An IR spectrum of the solution showed the presence of *cis*-$Ru(CO)_4I_2$ (ν-

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(CO) = 2195 (w), 2105 (vs), 2095 (s), 2067 (s) cm^{-1}), identified by comparison with the spectrum of an authentic sample,[8] and weak peaks indicating the presence of a small amount of $Ru_3(CO)_{12}I_6$ (ν(CO) = 2124 (m), 2065 (partially obscured), 2014 (s) cm^{-1}).[8] Similar reaction with even an excess of bromine at 0 °C yielded only *cis*-$Ru(CO)_4Br_2$ (ν(CO) = 2175 (m), 2133 (s), 2104 (s), 2071 (s) cm^{-1},[8] although $Ru_3(CO)_{12}Br_6$[8,9] (ν(CO) = 2133 (m), 2065 (s, br), 2009 (w) cm^{-1}) and $Ru_2(CO)_6Br_4$ (ν(CO) = 2132 (s), 2068 (vs), 2004 (m) cm^{-1}) were also formed as secondary products at higher temperatures.

Reaction of IV with Carbon Tetrachloride. A suspension of 0.2 g of IV in 10 mL of CCl_4 was refluxed under nitrogen for 96 h, after which time all of the starting material had gone into solution. An IR study showed that the solution contained $Ru_2(CO)_6Cl_4$[8-10] (ν(CO) = 2140 (m), 2082 (s), 2076 (vs), 2027 (m), 2018 (m) cm^{-1}), but no chloroform could be detected by GC. Similar treatment of III yielded the same compound.

Reaction of IV with Tertiary Phosphines. A suspension of 0.07 g (0.33 mmol of Ru) of IV in 30 mL of petroleum ether (bp 40–60 °C) containing 0.046 g (0.33 mmol) of PMe_2Ph was refluxed under nitrogen for 3 h. The resulting blood-red solution was shown (IR) to contain a mixture of $Ru(CO)_4(PMe_2Ph)$ (major, primary product; ν(CO) = 2062 (m), 1979 (m), 1949 (s) cm^{-1})[11] and $Ru(CO)_3(PMe_2Ph)_2$ (ν(CO) = 1897 cm^{-1}).[11] Similar products were formed with PMe_3, but no reaction occurred with PPh_3 even after refluxing for 6 days.

Discussion

As described in the Experimental Section, although photolysis of *dilute* solutions of $Ru_3(CO)_{12}$ (III) under 1 atm of CO results in the expected[3] formation of $Ru(CO)_5$ (I), similar treatment of *concentrated* solutions results in the preferential formation of a hitherto unidentified ruthenium carbonyl compound (IV). Elemental analyses are consistent with the formulation $[Ru(CO)_4]_n$, and the possible presence of a hydride ligand seems excluded by the observation that reaction of IV with refluxing carbon tetrachloride does not yield chloroform.[12]

The chemistry of IV duplicates that of III in many key ways. Thus, IV reacts with carbon monoxide to form a mixture of I and III; III reacts similarly to form I reversibly.[1] Compound IV also reacts with hydrogen to form $H_4Ru_4(CO)_{12}$. We have confirmed a report[7] that III does likewise, finding that the IR and NMR spectra of the compounds obtained from the two reactions are identical.

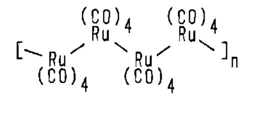
Reactions of IV with halogenating reagents also duplicate those of III. Iodine and bromine both react below room temperature to form the compounds *cis*-$Ru(CO)_4X_2$ (X = Br, I), as reported for III and confirmed by us, although the halide-bridged species $Ru_2(CO)_6X_4$ and $Ru_3(CO)_{12}X_6$ can also be formed as secondary products at higher tempertures. Similarly, the compound $Ru_2(CO)_6Cl_4$ is obtained on refluxing IV in carbon tetrachloride. It has been reported that III yields $Ru_2(CO)_6Cl_4$ on heating in chloroform,[13] and we obtain the same product on refluxing III in carbon tetrachloride.

Compound IV was also found to react with PMe_2Ph and PMe_3 (but not with PPh_3) to form compounds of the types $Ru(CO)_4L$ and $Ru(CO)_3L_2$ (L = PMe_2Ph, PMe_3). The tetracarbonyl species appear to be the primary products, and these are known to react rapidly with tertiary phosphines under the reaction conditions used to form the corresponding tricarbonyl compounds.[14] Reactions of III with all three tertiary phosphines occur under similar conditions, yielding cluster compounds of the type $Ru_3(CO)_9L_3$.[15]

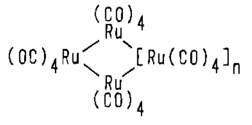
Compound IV is extremely insoluble in most solvents with which it does not react, and in spite of numerous attempts, we have been unable to grow crystals suitable for a single-crystal X-ray crystallographic study. Powder diffraction studies show, however, that the compound is crystalline. For the same reasons, attempts to obtain molecular weight measurements have proven fruitless as well. The compound is also extremely nonvolatile, and we have been unable to obtain useful mass spectral data. FAB-MS studies (suspensions in sulfolane, glycerol) were rather inconclusive, although peaks at *m/e* values possibly corresponding to $Ru(CO)_4^+$, $Ru_2(CO)_n^+$ (n = 1–8), $Ru_2C(CO)_n^+$ (n = 1–7), and Ru_n^+ (n = 1–5) were observed.

Compound IV is thus a tetracarbonyl compound of ruthenium, related to III chemically and, quite likely, structurally. As shown above, there are striking similarities between the reactions of IV and III with carbon monoxide, hydrogen, bromine, iodine, and carbon tetrachloride. We have carried out for purposes of comparison all of the relevant reactions of III, as reported in the literature, finding close correspondence with the chemistry of IV. In all cases, reaction mixtures and isolated products were characterized by utilizing a Bruker IFS 85 FTIR spectrometer equipped with an Aspect 2000 computer. Precision in measuring carbonyl stretching frequencies was very high, and compositions of mixtures were readily established by comparisons with literature data and, in some cases, by spectral subtractions. Thus, the nature and relative amounts of the products could be established with certainty.

The suggestion that IV is an isomer of III is supported by the observation that the solid-state IR spectra of III and IV are very similar (Figure 1). Although of relatively low resolution because of broadening inherent in the sampling of solids, the ranges of frequencies of the carbonyl stretching and bending modes of the two compounds are quite comparable, suggesting a similarity in the electron density on the ruthenium atoms in the two compounds. While the molecularity of IV is as yet unknown, its low solubility and volatility suggest polymeric or oligomeric structures, either linear (A) or cyclic (B). Interestingly, attempts to sublime IV resulted only in decomposition at about 126 °C to give a black material exhibiting no ν(CO) in its IR spectrum; no volatile, ruthenium-containing material was obtained. The existence of "open" clusters of either type, not based on a geometrical structure of high symmetry, appears not to have been reported previously.[16] However, such structures would appear to explain the lack of formation of cluster compounds in the reactions with tertiary phosphines, as occurs with III.[15] Quite possibly crystals of IV consist of a mixture of homologues of differing molecular weight; this hypothesis would explain the greater apparent broadening in the IR spectrum of IV. While far from definitive, the FAB-MS data are also consistent with the hypothesis of a polymeric or oligomeric structure.



A



B

As $Ru(CO)_5$ (I), once formed, decomposes to form $Ru_3(CO)_{12}$ (III) rather than IV, it seems likely that IV forms as a primary product during the photolysis of III, a process that has received attention from several groups. Thus, Wrighton et al.[17] have proposed the occurrence of homolytic fission to give the diradical C during the photocatalyzed isomerization of 1-pentene by III.

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(11) No attempt was made to separate the products, but the spectral data leave little doubt about their identity. For similar compounds, see: Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 32.2 and references therein.

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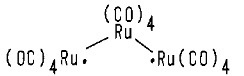

C

It was suggested that C was formed by excitation of an electron from a metal–metal bonding orbital into a metal–metal antibonding orbital.

However, two other groups[5,18,19] have found that the photogenerated species seems rather inert toward carbon tetrachloride, behavior unexpected of a diradical such as A, and have proposed carbonyl-bridged intermediates as alternatives. While we have little to offer in this continuing controversy,[20] we note that there appears to be a correlation between the relative amounts of I and IV that are formed and the initial concentration of III. Thus, IV is only obtained when the concentration of III is high, consistent with an oligomerization process. On this basis coupling of diradicals C would appear to be a reasonable route to a polymer or a cyclic oligomer containing repeating $[Ru_3(CO)_{12}]$ units.

As mentioned above, a compound appearing to be IV has been previously prepared in THF but not characterized.[4] We had initially assumed that the material reported and subsequently obtained by us was a THF adduct and hence was of little interest. It was only when we obtained it in hydrocarbon solvents as well that we suspected a new binary carbonyl compound. A similar material also appears to have been prepared by James et al.,[21] who obtained an insoluble purple solid formulated as $[HRu(CO)_3]_n$ from the carbonylation of aqueous solutions of ruthenium trichloride. We have repeated the synthesis of this material and found that it has an IR spectrum and an X-ray powder diffraction pattern similar to (but not identical with) the corresponding data for IV. We find that the purple solid reacts with iodine to form *cis*-$Ru(CO)_4I_2$ quantitatively, and as the original evidence for the hydride ligand was indirect, we suggest that the material obtained from aqueous solution is an isomer of IV.

Acknowledgment. We are indebted to the U.S. Office of Naval Research for support of this research. We also thank Johnson Matthey Ltd. and the International Nickel Co. of Canada for loans of ruthenium trichloride, Professor B. R. James for helpful comments, Professor R. D. Heyding for X-ray powder diffraction patterns, and Professors G. W. Wood and J. Holmes for mass spectra.

Registry No. I, 16406-48-7; III, 15243-33-1; IV, 29718-13-6; $H_4Ru_4(CO)_{12}$, 34438-91-0; *cis*-$Ru(CO)_4I_2$, 18475-75-7; *cis*-$Ru(CO)_4Br_2$, 21439-16-7; $Ru_2(CO)_6Br_4$, 22594-70-3; $Ru_2(CO)_6Cl_4$, 22594-69-0; $Ru(CO)_4(PMe_2Ph)$, 31447-09-3; $Ru(CO)_3(PMe_2Ph)$, 31447-08-2; $Ru(CO)_3(PMe_3)_2$, 75687-45-5; $Ru(CO)_4(PMe_3)$, 93180-37-1.

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Contribution from the Departments of Chemistry,
Birkbeck College, London WC1E 7HX, England,
and University College London, London WC1H 0AJ, England

Differentiation between Metal–Metal Stretching and Ligand-Sensitive Vibrations in Dimetal Tetraacetates by Ligand Deuteration

Andrew J. Hempleman,[1a,b] Robin J. H. Clark,*[1a]
and Colin D. Flint[1b]

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The assignment of metal–metal stretching vibrations in some dimetal tetraacetates remains controversial.[2-4] The main difficulty lies in the distinction between the metal–metal vibrations and the metal–oxygen vibrations since both may occur in similar spectral regions.[5] The most satisfactory method of assignment is to make use of the small shifts that occur on isotopic substitution of the metal atoms.[6,7] This method is, however, not generally applicable since suitable isotopes of some metals are not readily available and, in other cases, the cost may be prohibitive. The alternative procedure of ^{18}O substitution of the acetate grouping is also expensive.[5]

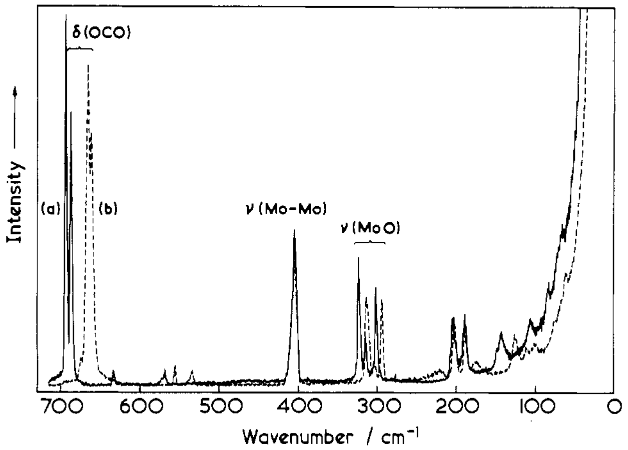

Figure 1. Raman spectra of (a) $Mo_2(O_2CCH_3)_4$ and (b) $Mo_2(O_2CCD_3)_4$.

In the course of our studies of the Raman, resonance Raman, and electronic spectra of dirhodium tetracarboxylates,[8,9] we observed that the wavenumber shifts in the metal–carboxylate modes induced by deuteration of the carboxylate ligand are larger than those caused by oxygen isotopic substitution. We were unable to confirm our assignments by metal isotope substitution since there are no stable isotopes of rhodium other than naturally occurring ^{103}Rh. It seemed possible that acetate deuteration would provide a low-cost, readily available, and generally applicable method for differentiation of predominantly metal–metal and metal–carboxylate stretching vibrations. In order to test this hypothesis, we have applied the method to the well-established case of $Mo_2(O_2CCH_3)_4$ where ν(Mo–Mo) has been shown to occur at 404 cm^{-1} by metal isotope substitution.[6]

Experimental Section

$Mo_2(O_2CCH_3)_4$ and its deuterated analogue were prepared by the method of Holste et al.[10] Acetic-d_3 acid-d (99.96%) was obtained from Aldrich Chemical Co., Inc. The samples for Raman spectroscopy were mounted as pressed disks side by side in the cryostat and measured under identical conditions (sample temperature 20 K with <3 mW of 5145-Å excitation at a spectral slit width of 2 cm^{-1}) to ensure equal temperatures. Infrared spectra were measured at 80 K as pressed wax disks at a spectral resolution of 1 cm^{-1} with a Bruker 113 V interferometer.

Results

The 20 K Raman spectra of $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCD_3)_4$ are shown in Figure 1, and the wavenumbers of the prominent features below 450 cm^{-1} are given in Table I. It is immediately clear that the band at 404 cm^{-1} is essentially unshifted on deuteration whereas the group of three bands in the 323–301-cm^{-1}

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