Figure 2. IR spectrum of the product of the preparative-scale Ru + CO matrix isolation reaction performed at 30 K, extracted under Ar with pentane at 200 K, and recorded at (A) 3 min, (B) 71 min, (C) 196 min, (D) 431 min, and (E) 1478 min after reaching room temperature, depicting the gradual transformation from Ru(CO)$_5$, denoted 1, to Ru$_3$-(CO)$_{12}$, denoted 3.

duction rates of MVS-based materials.

Results and Discussion

The synthesis of Ru(CO)$_5$ is a good first test of the method for a number of reasons. First, Ru is a refractory metal requiring a rather high temperature for its evaporation at an acceptable rate (2300 K) and at the same time minimizing radiation heating of the cryoshield from the evaporant to establish a deposition temperature of less than 30 K. Second, UV–visible radiation from the hot source has to be minimized in order to cut back on the photochemically induced conversion of Ru(CO)$_5$ to Ru$_3$(CO)$_{12}$. To achieve the latter required appropriately positioned radiation shields between the e-gun (D) and the reaction zone (B). Third, while the traditional preparation of Ru$_3$(CO)$_{12}$ is relatively straightforward,[7] the synthesis of thermally labile Ru(CO)$_5$ in a pure form is fairly demanding.[8]

The cocondensation of Ru atoms and CO at 30 K gave a white matrix which on warming to 200 K and dissolving in pentane produced a colorless solution. An IR spectrum of the product after 3 min at room temperature exhibits strong ν_{CO} absorptions at 2037 and 2003 cm^{-1} (labeled 1 in Figure 2) attributable to the desired product, Ru(CO)$_5$.[8] On retaining at room temperature under Ar, the initially colorless solution gradually transforms to a deep orange. The corresponding changes in the IR spectrum shown in Figure 2 depict the conversion of essentially pure Ru(CO)$_5$ to Ru$_3$(CO)$_{12}$.[7] After 24 h the change is complete as seen by Ru$_3$(CO)$_{12}$ ν_{CO} IR bands at 2061, 2031, and 2012 cm^{-1}, denoted 3 in Figure 2.

The synthesis of Mn$_2$(CO)$_{10}$ is also a good test of the method because the best reported preparation[9] of this material is regarded as difficult and time-consuming. In our experiments a purple matrix was obtained on cocondensing Mn atoms and CO at 25 K (possibly containing Mn(CO)$_5$), which on warming to room

temperature yielded an orange-brown solid. Extraction and sublimation gave pure Mn$_2$(CO)$_{10}$ as yellow crystals with characteristic IR ν_{CO} bands at 2047 (s), 2016 (vs), and 1985 (s) cm^{-1} and UV–vis absorptions at λ_{max} 400 (sh), 341 (s), and 210 (s) nm.[10,11]

In the remaining part of this report we will briefly describe the MVS of three other well known carbonyls, simply to demonstrate the routine nature of the preparative-scale matrix isolation experiment.

Thus, cocondensing V atoms with CO at 28 K under mononuclear reaction conditions yields a blue-green matrix, which after slow warming to room temperature followed by pentane extraction of the remaining blue-green solid yields pure V(CO)$_6$:[10] IR ν_{CO} 1975 cm^{-1}. No evidence was found at room temperature for the V$_2$(CO)$_{12}$ dimer observed in corresponding MIS experiments.[12]

Cr atoms cocondensed with CO at 28 K give after removal of excess CO a tan solid, which after extraction and sublimation yielded white crystals of pure Cr(CO$_6$):[10] IR ν_{CO} 1986 cm^{-1}, ν_{CrC} 440 cm^{-1} (pentane solvent); mass spectrum m/e 220 (M$^+$).

Finally, cocondensation of Fe atoms at a high rate with CO at 28 K favoring cluster reaction conditions[1] yielded a green matrix from which a green solid could be extracted at room temperature in pentane. Sublimation affords green crystals of Fe$_3$(CO)$_{12}$: IR ν_{CO} 2046 (s), 2026 (m), 2004 (sh) cm^{-1} (pentane solvent).[10] The lower nuclearity Fe(CO)$_5$ and Fe$_2$(CO)$_9$ products expected to also form in this reaction were not purified or analyzed in the workup procedure.

In summary, the work described in this paper demonstrates the viability of preparative-scale matrix isolation using metal atomic reagents, as exemplified by successful single-step syntheses of Ru(CO)$_5$, Ru$_3$(CO)$_{12}$, Mn$_2$(CO)$_{10}$, V(CO)$_6$, Cr(CO)$_6$, and Fe$_3$-(CO)$_{12}$. Advantages here relate to the simplicity of the synthesis, ease of purification of the products, extensions to any metal, and direct incorporation of $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopically labeled ligands, as well as isotopically pure metals.

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Multielectron-Photoinduced Reduction of Chloroplatinum Complexes: Visible Light Deposition of Platinum Metal

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The ability to either deposit platinum metal under spatially well-defined conditions or generate a well-characterized platinum colloid is of interest to research in the areas of heterogeneous

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catalysis and electronic devices. To this end, photochemically induced reduction of simple platinum complexes in aqueous solution to platinum metal offers an approach that can be carried out under mild and thus controllable conditions. However, there exist few reports on the four-electron photoreduction of Pt(IV) complexes.[1,2] On the other hand, Pt(II) complexes tend to be easily thermally reduced, removing the synthetic control available via a pure photochemical reaction scheme. We have thus undertaken an investigation of the aqueous redox photochemistry of $PtCl_6^{2-}$ in the presence of alcohols in order to investigate photochemical pathways that might lead to multiple-electron-reduced products. In so doing we report for the first time on the four-electron reduction of a $PtCl_6^{2-}$ complex using low-energy visible photons. The metal so generated is obtained as either a colloid or a mirror depending on reaction conditions. Further, under high concentrations of $PtCl_6^{2-}$ or Cl^-, the reduction is found to stop at the two-electron stage, revealing an efficient method of synthesizing $PtCl_4^{2-}$ from $PtCl_6^{2-}$.

Experimental Section

All chemicals were reagent grade and used as received. $PtCl_6^{2-}$ was obtained either as the diacid, potassium salt, or sodium salt. All species were tested in order to determine possible cation (and pH) effects on the reaction. (None were observed.) $PtCl_4^{2-}$ was employed as the potassium salt.

Photolysis reactions were carried out with a beam-expanded argon ion laser source (Spectra Physics 164). Incident light intensities and photons absorbed were determined by using a Newport Research Model 815 power meter rated ±5% NBS traceable. Organic products were analyzed by using a Perkin-Elmer Sigma 3B dual FID gas chromatograph with a 3% Carbowax 20M 80/100 Cromosorb WHP column. Quantitative analysis was accomplished with cyclohexanone as an internal standard. Platinum species were detected by using a Bruker 250-MHz FTNMR to obtain ^{195}Pt NMR spectra.[7,8] Samples to be studied by NMR were prepared as follows. Na_2PtCl_6 was dissolved in a 1:9 D_2O:2-propanol mixture (by volume) to generate 3.5 mL of a 15.2 mM $PtCl_6^{2-}$ solution. $PtCl_6^{2-}$ in ethanol or 2-propanol yields a singlet in its ^{195}Pt NMR spectrum, which we have employed as the reference signal. The NMR spectrum of $PtCl_4^{2-}$ is composed of a singlet 1620 ppm upfield from that of $PtCl_6^{2-}$. Quantitative analysis of ^{195}Pt NMR data is justified by linear plots for concentration of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ (<16 mM) vs. their peak integral areas using 3.50-mL samples and 512 scans. Concentration vs. NMR signal studies were also carried out for $PtCl_4^{2-}$ in the presence of $PtCl_6^{2-}$. Mixtures of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ have previously been reported to generate a Pt(III) species according to the equilibrium[9,10]

$$2PtCl_5^{2-} \rightleftharpoons PtCl_6^{2-} + PtCl_4^{2-} \qquad (1)$$

The presence of paramagnetic $PtCl_5^{2-}$ was of concern since possible line broadening and peak shifts could have destroyed the analytical utility of the NMR technique in experiments where photolysis of Pt(IV) led to the generation of Pt(II). The control experiments, however, indicated no line broadening or frequency shifts in mixtures of $PtCl_6^{2-}/PtCl_4^{2-}$. Integrated peak areas were found to be less than those found when only one oxidation state was present. We associated this variation with the formation of NMR-silent platinum complex.

(1) Vogler, A.; Hlavatsch, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.
(2) Bard[3] has reported that $[Pt^{IV}Cl_6]^{2-}$ can be photoreduced to platinum metal by intense ultraviolet light photolysis in the presence of an organic acid. There is, however, some question as to whether or not the processes are photochemical since Karlicek[4] has recently noted that the laser-induced reduction of $[PtCl_6]^{2-}$ to metal in an aqueous methanolic solution is a purely thermal process.
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(7) ^{195}Pt NMR has previously been shown to have good sensitivity to variations in the ligand sphere and metal oxidation state.[8] The technique has been found analytically useful in following the kinetics of $PtCl_4^{2-}$ aquation.[8a]
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(9) No NMR line broadening is observed upon photolysis, consistent with the control experiments (see Experimental Section).
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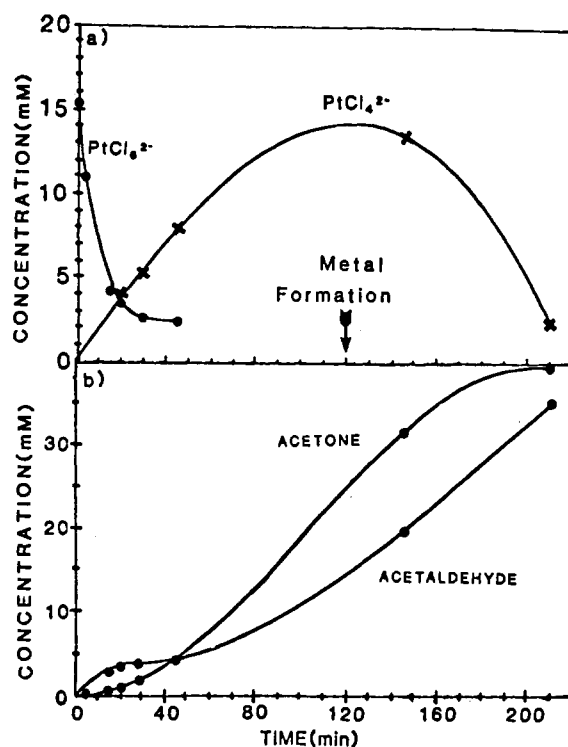
Figure 1. Time dependence of $[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, acetone, and acetyldehyde concentrations during the photoreduction (0.062 W, 488 nm) of 3.5-mL Na_2PtCl_6 (15.3 mM) solution in a 1:9 D_2O:2-propanol mixture (by volume).

UV–visible spectroscopy (HP 4850) was employed to ascertain the integrity of the ligand sphere and the concentration of Pt(II), as an independent check on the NMR data. The kinetics of $PtCl_4^{2-}$ reduction were established by monitoring absorption at 478 nm. To obtain the time dependence of the $PtCl_4^{2-}$ reduction, the reaction was quenched at various times with KCl. As discussed in the text, this is an efficient means of inhibiting the chemistry of interest.

In a typical experiment 3.5 mL of an alcohol solution that was 15 mM in H_2PtCl_6 was irradiated with 488-nm light (10–100 mW) for times ranging from several minutes to several hours. after irradiation samples were immediately analyzed as discussed above. Dark controls were also carried through the analysis.

Results and Discussion

The four-electron-photoinduced reduction of $PtCl_6^{2-}$ in aqueous alcohol does not require heating and occurs at all wavelengths at which the complex absorbs light.[5] Thus, irradiation at energies as low as 514 nm, reported to excite a $PtCl_6^{2-}$ $^1A_{1g} \rightarrow ^3T_{1g}$ ligand-field transition,[6] yields platinum metal. Analysis of the organic products formed during the reduction of $PtCl_6^{2-}$ indicates that the photoinduced platinum redox reaction oxidizes primary alcohols to aldehydes; however, secondary alcohols are found to produce a mixture of ketones and organic products associated with alkyl loss. For example, if a solution of H_2PtCl_6 in ethanol is irradiated with 488-nm light, acetaldehyde is found as the only observable organic product. However, 488-nm irradiation of a 15.3 mM solution of H_2PtCl_6 in 2-propanol yields acetone and acetaldehyde. The reactions of $PtCl_6^{2-}$ with ethanol and 2-propanol are prototypical[5] and have been employed herein to characterize the platinum photoredox chemistry.

Figure 1 details the time dependence of the NMR-sensitive platinum species during the photoreduction of $PtCl_6^{2-}$ by 2-propanol, along with organic product formation as determined by gas chromatography. As can be seen from these data the initially observed platinum photoproduct is $PtCl_4^{2-}$. There exists a fairly long induction period prior to metal formation. The exact length of this period depends on the light intensity employed and the reagent concentrations. Just prior to metal formation the amount of $PtCl_4^{2-}$ observed quantitatively accounts for the disappearance of $PtCl_6^{2-}$; however, at earlier times the sum of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ is less than the initial value of $PtCl_6^{2-}$. Similarly it

$$K_2PtCl_4 + HOET_{(excess)} \xrightarrow{dark, H_2O} Pt^0 + H\overset{O}{\overset{\|}{C}}CH_3 + 2HCl + 2KCl$$
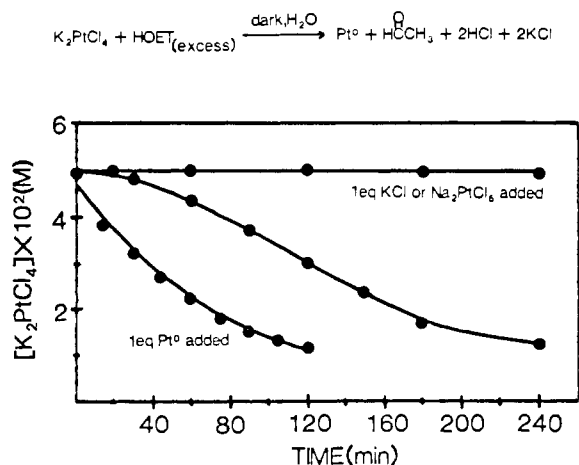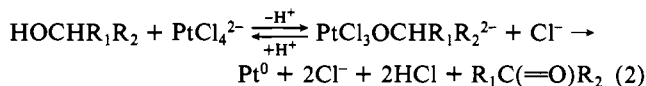

Figure 2. Time dependence of K_2PtCl_4 concentration during the dark reduction of 0.24 g of K_2PtCl_4 (6.05 mM) in 10.7 mL of H_2O and 0.85 mL of ethanol (25 equiv) at 25 °C in a 50-mL flask. The middle trace indicates the response of the native system, while the top trace shows the inhibition associated with addition of $PtCl_6{}^{2-}$ (or Cl^-) and the bottom trace shows the catalytic activity of platinum metal.

is found that the initial quantum yield for $PtCl_6{}^{2-}$ disappearance (0.32 at 488 nm)[9b] is 4 times greater than the initial $PtCl_4{}^{2-}$ appearance quantum yield (0.074 at 488 nm). This inconsistency can be attributed to the equilibrium formation of $Pt(III)^9$ via coupling of the Pt(II) and Pt(IV) complexes (reaction 1), as previously discussed by Taube[10] and Lawrence.[11] Alternatively, the Pt(III) species might be directly generated during the oxidation of the alcohol via a one-electron charge-transfer mechanism. Further evidence for the role of Pt(III) is presented later. Once an initial amount of metal is produced, the reaction rapidly goes to completion. Control experiments indicate no dark reactivity.

In general, platinum metal formation is not found to occur until a ~90% yield of $PtCl_4{}^{2-}$ has accumulated. This suggests that $PtCl_6{}^{2-}$ acts as an inhibitor to platinum metal formation. In order to gain insight into this process, the reduction chemistry of $PtCl_4{}^{2-}$ has been examined. $PtCl_4{}^{2-}$ reacts with ethanol in a thermal redox reaction to produce platinum metal. The kinetics of this reaction are illustrated in Figure 2. It is observed from these data that a simple rate law is not operational. Gas chromatographic analysis of the organic products indicates the quantitative formation of acetaldehyde at a rate of 1 equiv/equiv of $PtCl_4{}^{2-}$ consumed. Addition of $PtCl_6{}^{2-}$ (or KCl) has a strong inhibiting effect on metal formation, demonstrating the source of the $PtCl_6{}^{2-}$ inhibition. On the other hand, it can be seen from data in this figure that platinum metal catalyzes the reaction, yielding first-order kinetics of $PtCl_4{}^{2-}$ with an observed rate constant of 1.1×10^{-4} s^{-1}. This catalysis may be associated with the previously observed capability of platinum metal to enhance charge-transfer rates between metal redox couples.[12] Alternatively, the effect may be related to the lattice stabilization energy available once platinum nuclei are established. The autocatalytic nature of platinum metal in combination with $PtCl_6{}^{2-}$ inhibition thus gives rise to the observed rapid formation of metal once the initial induction period is completed.

The strong inhibitory effect of $PtCl_6{}^{2-}$ can be accounted for in a number of ways. One possibility is that a Pt(III) species is generated according to reaction 1. If this mechanism is solely responsible for the observed inhibition, then replacement of $PtCl_6{}^{2-}$ with KCl is not expected to duplicate this effect. Alternatively, the inhibition might be associated with a chloride substitution mechanism, in which either free chloride or $PtCl_6{}^{2-}$ binds to $PtCl_4{}^{2-}$, thus blocking EtOH ligation.[13] Independent of the exact
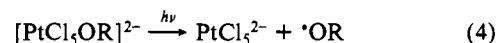
mechanism, these data suggest that the reversible substitution of a chloride ligand on $PtCl_4{}^{2-}$ by alcohol must occur prior to reduction of $PtCl_4{}^{2-}$. β-Hydride elimination would ultimately lead to formation of Pt^0 and the carbonyl product; this has been directly observed for the reaction of $(PPh_3)_2 \ PtCl_2$ with alcohol.[15]

$$HOCHR_1R_2 + PtCl_4{}^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} PtCl_3OCHR_1R_2{}^{2-} + Cl^- \rightarrow$$
$$Pt^0 + 2Cl^- + 2HCl + R_1C(=O)R_2 \quad (2)$$

The stoichiometry of reaction 2 is supported by a 94% yield of acetone when a 4 mM solution of K_2PtCl_4 with 1 equiv of 2-propanol in H_2O reacts under dark conditions. The necessity of a proton on the α-carbon is demonstrated by a lack of reactivity when *tert*-butyl alcohol is employed as the reducing agent.

Reaction 2 also has a strong photochemical component that is sensitive to irradiation into both $PtCl_4{}^{2-}$ ligand-field and charge-transfer bands. For example, the initial velocity for $PtCl_4{}^{2-}$ disappearance in the absence of platinum metal increases from its dark value of 1.7×10^{-6} to 1.0×10^{-5} M s^{-1} with an initial quantum yield of 0.16 if the reaction is irradiated with 85 mW of 488-nm light. Previous studies have shown that irradiation of $PtCl_4{}^{2-}$ leads to population of the ^3E_g state, producing ligand substitution via an associative mechanism.[14] Similarly, light may also accelerate the substitution step of reaction 2. Interestingly, the quantum yield for $PtCl_4{}^{2-}$ disappearance noted here is the same value as previously noted for the photoinduced aquation of $PtCl_4{}^{2-}$.[15] Whether light influences the β-hydride elimination step is not clear.[16]

Unlike the case of $PtCl_4{}^{2-}$ reduction, which only yields acetone as the organic product, acetaldehyde is initially the major product during the photoreduction of $PtCl_6{}^{2-}$ by 2-propanol. As shown in Figure 1b after 15 min of reaction the ratio of [acetaldehyde] to [acetone] equals 8.5. The loss of methyl necessary to transform 2-propanol to acetaldehyde is diagnostic for a free-radical mechanism.[17] Under thermodynamic control the one-electron oxidation of 2-propanol results in H$^\bullet$ loss and the formation of an α-carbon-based free radical. This species then reacts to form acetone. $CH_3{}^\bullet$ loss can only occur if an oxygen-based free radical is generated (i.e., the reaction is under kinetic control). A one-electron oxidation of alcohol to produce the alkoxy radical may be achieved by photogeneration of $Cl^\bullet$ via a $PtCl_6{}^{2-}$ charge-transfer-excited state. Charge-transfer photochemistry upon irradiation into the d–d bands of the $PtCl_6{}^{2-}$ absorption spectra has previously been noticed.[18] As considered by Tobe for the photooxidation of Cl^- by $PtCl_6{}^{2-}$,[19] oxidation of alcohol might also occur via a direct outer-sphere charge transfer from $PtCl_6{}^{2-*}$. Both of these mechanisms should lead to a carbon-based free radical, however, and therefore only can account for acetone production. On the other hand, if the initial photoprocess involves Cl^- loss from a ligand-field-excited state, a Pt(IV) alkoxide could be generated.[18] Absorption of a second photon by this complex might cause homolytic cleavage of the platinum–oxygen bond to generate the necessary oxygen-based organic free radical:

$$[PtCl_6]^{2-} + ROH \xrightarrow{h\nu} [PtCl_5OR]^{2-} + HCl \quad (3)$$

$$[PtCl_5OR]^{2-} \xrightarrow{h\nu} PtCl_5{}^{2-} + {}^\bullet OR \quad (4)$$

Concomitant with production of the organic free radical, a Pt(III) species is generated (reaction 4), consistent with the NMR data presented. Pt(III) may then disproportionate to form $PtCl_4{}^{2-}$ and $PtCl_6{}^{2-}$ according to reaction 1. As the reaction coordinate proceeds, $PtCl_6{}^{2-}$ is consumed, reducing the rate of reactions 3 and 4 while increasing the rate of reaction 2. This second reaction

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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 $PtCl_6^{2-}$.

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.

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A New Form of Ruthenium Tetracarbonyl

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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 $RuCl_3\cdot3H_2O$ 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
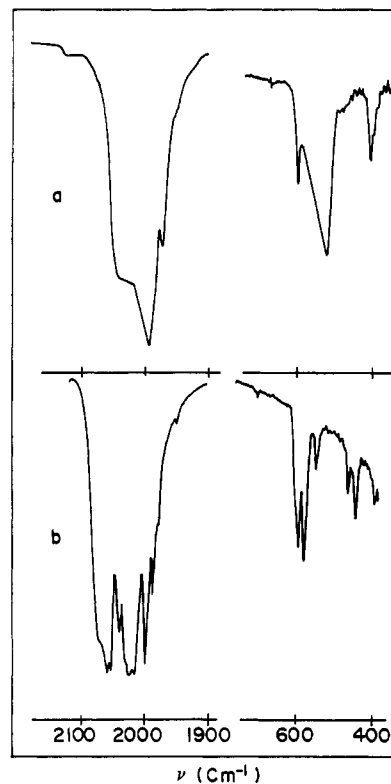
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Figure 1. IR spectra (KBr disks) of $[Ru(CO)_4]_n$ (a) and $Ru_3(CO)_{12}$ (b).

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.

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 ($\nu(CO)$ = 2037 (s), 2002 (vs) cm^{-1}) and III ($\nu(CO)$ = 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 ($\nu(CO)$ = 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-

(7) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.