of cyclopentadienyl derivatives, exhibits the lowest ^{51}V shielding.

Registry No. **1**, 98759-88-7; **2**, 102782-28-5; **3**, 84270-55-3; **4**, 102782-29-6; **5**, 102747-46-6; **6**, 102747-47-7; **7**, 63339-27-5; $C_5Me(Cy)H_4$, 102782-30-9; $C_5Me(cetyl)H_4$, 102782-31-0; $C_5(trityl)H_5$, 62790-43-6; C_5H_6, 542-92-7; C_5MeH_5, 26519-91-5; C_4Br, 108-85-0; C_4Cl, 542-18-7; (cetyl)Br, 112-82-3; (trityl)Cl, 76-83-5; $V(CO)_6$, 14024-00-1; $Na(diglyme)_2V(CO)_6$, 15531-13-2; H_3O_4P, 7664-38-2.

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Preparative-Scale Matrix Isolation: Application to the Direct Synthesis of Binary Metal Carbonyls Using Metal Atomic Reagents

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Received January 31, 1986

Many highly labile organometallics accessible by metal vapor synthesis (MVS) are potentially interesting precursors for the fabrication of supported metal clusters, colloids, islands, and films under extremely mild conditions. Gram-scale syntheses using metal vapor reagents were pioneered by the groups of Timms[1] and Skell[2] using ligands that are condensable at 77 K, the temperature of liquid nitrogen. Such syntheses, however, have not been possible on the gram scale with ligands that are noncondensable at 77 K, e.g. N_2, O_2, H_2, CO, CH_4, NO, C_2H_4, etc. This class of ligand and their compounds have remained the curiosity of matrix isolation spectroscopists (MIS).[3] One obvious reason was the need to use and pay for liquid helium. Another obstacle of a more chemical nature related to the fact that at 77 K competitive metal atom diffusion/agglomeration processes in these volatile ligands overwhelm the desired metal–ligand complexation reaction. Here one generally obtains colloidal metal compositions rather than well-defined compounds. When the temperature is lowered below about one-third of the melting point of the ligand (the Tamman temperature,[1,4] below which metal atom diffusion in the solid matrix is minimized), metal–ligand complexation predominates over that of metal atom aggregation. A case in point is the temperature dependence of the nickel atom–dinitrogen reaction[5]

which requires the lower temperature for complex formation even though the decomposition temperature of $Ni(N_2)_4$ has been estimated to be about 80–100 K.[6] With a judicious choice of metal atom concentration, ligand, deposition rate, and temperature, the yield of a desired M_xL_y compound can be optimized.

We have developed a reactor system and techniques for performing preparative-scale MVS experiments using the so-called noncondensable ligands. Although these require sub-77 K conditions for synthesis of their metal complexes, they often display supra-77 K decomposition temperatures, making them attractive organometallic synthons and precursors for the production of novel kinds of supported metal compositions.

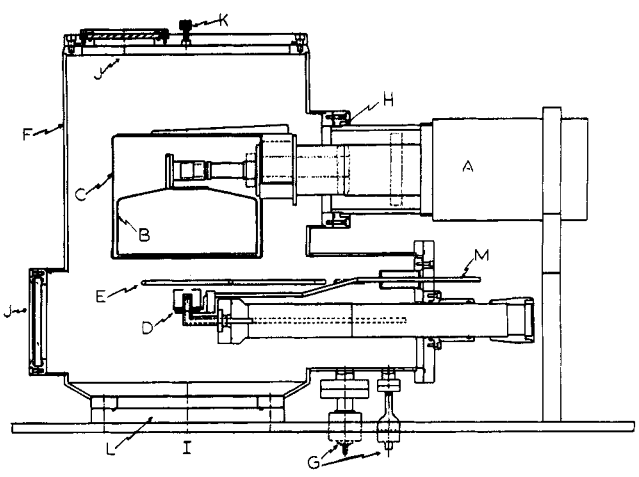

Figure 1. Preparative-scale matrix isolation equipment for conducting metal vapor synthesis over the extended temperature range 15–300 K. Figure notation: (A) high-refrigeration-capacity cryopump (Air Products); (B) reaction cryoshield on first stage (4 W at 10 K); (C) radiation shield on 77 K second stage (70 W at 77 K); (D) reverse-polarity, electrostatically focused, quartz-crystal, mass-monitored (resolution 20 ng), 3.5-kW electron gun; (E) mass-flow-controlled ligand inlet (Vacuum General); (F) stainless-steel vacuum chamber; (G) cold-cathode, thermocouple vacuum gauges (Varian); (H) rotation seal for cryopump; (I) high-capacity diffusion pump (Edwards, 2300 L s^{-1}); (J) observation windows; (K) arrangement of temperature-controlled Schlenk cannulas; (L) pneumatic slide valve (Airco); (M) electron gun liquid-N_2 cryoshield.

This report describes the direct synthesis of a number of mononuclear and cluster metal carbonyls, which represents our model system for evaluating the viability of a preparative-scale matrix isolation experiment.

Experimental Section

The cocondensation of the monatomic vapors of V, Cr, Mn, Fe, and Ru (generated from a reverse-polarity, electrostatically focused, quartz-crystal, mass-monitored, 3.5-kW electron gun) with CO (Matheson Research Purity) at 20–30 K in a quantitative fashion (mass resolution 20 ng) requires the use of a fairly high-capacity closed-cycle helium refrigerator (4 W at 10 K, 70 W at 77 K, Displex 204) as the reaction chamber, configured as shown in Figure 1. The cocondensation reaction typically involved deposition of 10–100 mg of metal vapor with 10–100 g of CO during a period for 1–6 h onto a copper reaction shield maintained below 30 K by the cryostat under a dynamic vacuum of below 10^{-5} torr. After deposition, the cryoshield is rotated through 180° and slowly allowed to warm (sometimes under Ar) to remove unreacted CO (Figure 1). Subsequently, the product is dissolved in a suitable solvent (pentane or toluene, distilled from sodium benzophenone ketyl) and removed through the top flange of the reaction chamber via a triple-walled temperature-controlled (77–300 K) cannula, to a flask where standard purification steps (removal of solvent and sometimes sublimation) are performed on a Schlenk line. In this preliminary study the yields were not optimized but generally exceeded 60% based on the quantity of metal condensed on the copper reaction shield. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrometer and UV–vis spectra on a Perkin-Elmer 330 spectrometer.

This study demonstrated that a higher refrigeration capacity reaction chamber must be realized to increase the production of materials to the gram scale during a reasonable deposition period of 3–4 h. This would eliminate the formation of a "gas window" caused by low condensation rates of CO at the copper reaction shield during high gas depositions, leading to reduced yields of metal atoms arriving at the reaction shield. An adjustable distance between the electron gun (D) and the reaction shield (B) would help alleviate this difficulty. In this regard it is informative to compare the closed-cycle helium refrigerator to a liquid-helium cryostat. Considering only the cooling capacities of the two types of refrigeration methods and maintaining similar reaction shield and equipment design, we estimate that the capital cost of the closed-cycle system is recovered after about 200 runs when compared solely to the cost of liquid helium. However, in the event that commercial high-capacity cryopumps (e.g. 100 W or more at 10–30 K) are not forthcoming in the near future, it may prove necessary to move to a new reactor design incorporating liquid-helium cooling, in order to achieve practical pro-

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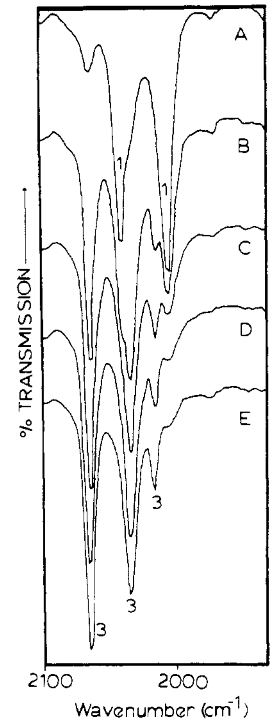

Figure 2. IR spectrum of the product of the preparative-scale Ru + CO matrix isolation reaction performed at 30 K, extracted under Ar with pentane at 200 K, and recorded at (A) 3 min, (B) 71 min, (C) 196 min, (D) 431 min, and (E) 1478 min after reaching room temperature, depicting the gradual transformation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

Acknowledgment. The financial assistance of the Natural Sciences and Engineering Research Council of Canada's Operating and PRAI Grants Programmes are greatly appreciated. Also, the award of a 3M scholarship to G.A.O. is acknowledged. The technical assistance of Karl Molnar and Wolfgang Panning proved to be invaluable. Stimulating discussions with Dr. Mark Andrews and Dr. Robin Whyman were most helpful in the development stages of this project. Laboratory assistance from Kate Helwig is also acknowledged with gratitude.

Registry No. $Ru(CO)_5$, 16406-48-7; $Ru_3(CO)_{12}$, 15243-33-1; $Mn_2(CO)_{10}$, 10170-69-1; $V(CO)_6$, 14024-00-1; $Cr(CO)_6$, 13007-92-6; $Fe_3(CO)_{12}$, 17685-52-8.

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

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Received July 31, 1985

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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