hexasolventocopper(II) ion in acetic acid is very fast, as expected from the Jahn–Teller effect of the copper(II) ion,[2] while the solvent-exchange rate on the copper acetate is much slower, since the latter forms the dimeric structure and the solvated acetic acid molecules at its axial sites are stabilized by hydrogen bonding as depicted in I.

Acknowledgment. The present work was supported through a Grant-in-Aid for Scientific Research (No. 59430010) and a Grant-in-Aid for Special Project Research (No. 60129031) from the Japanese Ministry of Education, Science, and Culture.

Registry No. HOAc, 64-19-7; $Mn(OAc)_2$, 638-38-0; $Co(OAc)_2$, 71-48-7; $Cu_2(OAc)_4$, 23686-23-9.

Supplementary Material Available: Oxygen-17 line-broadening data for $Mn(OAc)_2$, $Co(OAc)_2$, and $Cu_2(OAc)_4$ in acetic acid and in mixtures with CD_2Cl_2 (Table s-I), proton line-broadening data for $Mn(OAc)_2$ in an acetic acid–CD_2Cl_2 mixture (Table s-II), and values of ΔH^*, ΔS^*, C_M, E_M, C_O, E_O, and C_ω (Table s-III) (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Hamburg, D-2 Hamburg 13, FRG

Ring-Substituted Derivatives of η^5-$C_5H_5V(CO)_4$: Synthesis and ^{51}V NMR Spectroscopic Characteristics

Martin Hoch, Andreas Duch, and Dieter Rehder*

Received February 12, 1986

In a recent paper,[1] Basolo and co-workers described the synthesis and molecular structure of η^5-$C_9H_7V(CO)_4$ (**1**) (C_9H_7 = indenyl), obtained in 40% yield from the reaction of $[V(CO)_6]^-$ and C_9H_7HgCl. We have found that the direct action of the neutral 17-electron complex $V(CO)_6$ on indene produces **1** in about 70% yield. This reaction, which possibly runs via an intermediate "$HV(CO)_6$",[2] can more generally be applied to the synthesis of other ring-substituted cyclopentadienyl complexes in yields of 55–85% and thus opens a route to this little known class of compounds alternative to the hydride transfer from phosphine-stabilized hydridocarbonylvanadium complexes to the exocyclic carbon of pentafulvenes.[3] Ring-substituted derivatives of $C_5H_5V(CO)_4$ are of considerable interest in the context of the stabilization of the labile $C_5H_5V(CO)_3THF$, an excellent precursor for the synthesis of a large variety of substitution products $C_5H_5V(CO)_3L$.[4]

Experimental Section

All operations were carried out under nitrogen and in oxygen-free, absolute solvents. Bis(cyclopentadienes), as far as available commercially ($(C_5H_6)_2$, $(C_5Me_5)_2$, $(C_5(Et)Me_4H)_2$, $(C_5Me_5H)_2$) and indene were purified by distillation. Silica gel (Kieselgel 60, Merck, 70–230 mesh ASTM) was pretreated in vacuo (8 h, 1–2 Torr) and loaded with N_2.

Preparation of Alkylcyclopentadienes. The equivalent of 2.4 g of sodium hydride (77 mmol) of a paraffin oil suspension of NaH was washed twice with 20-mL portions of light petroleum ether, dried in vacuo, treated with 100 mL of THF, and cooled in an ice bath. A 77-mmol sample (ca. 5 g or 6.4 mL) of freshly distilled $C_5(R)H_5$ (R = H, Me) was added so as to keep the evolution of H_2 at a moderate rate. In case the solution was still turbid, further cyclopentadiene was added in small portions until clearing. To this colorless to pink solution was added 65 mmol of alkyl halide (CyBr or CyCl, (cetyl)Br, (trityl)Cl). After ca. 2 h of refluxing, the yellow to light red solution was evaporated, the remaining oil or paste redissolved in 100 mL of diethyl ether, and the resultant solution washed four times with 10-mL portions of water. The organic phase was then dried over $MgSO_4$ and the ether removed by distillation. Workup of the residual products was carried out by fractional distillation ($C_5Me(Cy)H_4$, 80–85 °C at 15–18 Torr; yield 60%), by filtration of the ether solution through a 6-cm layer of silica gel ($C_5Me(cetyl)H_4$;[5] yield 85%), or by recrystallization from petroleum ether[6] ($C_5(trityl)H_5$; yield 85%). Only the cyclohexyl derivative tends to dimerize.

Table I. Yields and Selected Properties of η^5-$Cp'V(CO)_4$ Complexes

complex	Cp′[a]	yield, %	properties
1	indenyl	69	orange crystals
2	$C_5(trityl)H_4$	85	yellow crystals
3	C_5Me_5	73	orange powder
4	$C_5(Et)Me_4$	72	orange powder
5	$C_5Me(cetyl)H_3$	58	light yellow wax
6	$C_5Me(Cy)H_3$	54	orange crystals
7	C_5MeH_4	76	orange oil

[a] Abbreviations: indenyl = C_9H_7, trityl = $C(C_6H_5)_3$, cetyl = n-$C_{16}H_{33}$, Cy = c-C_6H_{11}.

$V(CO)_6$ was obtained in 91% yields by reacting 9-g portions of $Na(diglyme)_2V(CO)_6$ (Ventron) with 18 g of orthophosphoric acid, intimately mixed in a sublimation apparatus. $V(CO)_6$ sublimes from this mixture at 50 °C and 0.01 Torr.

η^5-$Cp'V(CO)_4$. In a typical experiment, 310 mg (1.4 mmol) of $V(CO)_6$, dissolved in 25 mL of *n*-hexane, was treated with 1.7 mmol of the freshly distilled cyclopentadiene and the mixture refluxed for 2 h. Direct sunlight was avoided. In *n*-pentane, reaction times are about 3 times as long. Small amounts of vanadium metal and $[Cp'_2V(CO)_2][V(CO)_6]$ were filtered off. The filtrate, appearing orange or green (the latter due to suspended vanadium particles) and containing $Cp'V(CO)_4$ and $(HCp')_n$ (^1H NMR evidence), was evaporated to yield an oil. This was dissolved in 1 mL of THF and chromatographed on silica gel with pentane as elutant (column dimensions 10 × 25 cm; ca. 60 mL of pentane; elution time ca. 1 h). After removal of the pentane by vacuum evaporation at room temperature, the complexes were obtained in a pure form and with satisfactory elemental analyses. Yields and some of the properties of the new compounds are given in Table I.

Results and Discussion

The compounds described in this work and obtained according to eq 1 are given in Table II together with their characteristic vanadium-51 NMR shifts and CO stretching frequencies. In

$$V(CO)_6 + HCp' \rightarrow Cp'V(CO)_4 + 2CO\ (+{}^1/{}_2H_2) \quad (1)$$

contrast to findings on (acetyl–C_5H_4)$V(CO)_4$[7] and various (alkenyl–C_5H_4)$V(CO)_4$ complexes,[2] **3**, **4**, **6**, and **7** show two IR-active bands only. The B_1 mode, which should gain intensity as the overall C_{4v} symmetry of the parent cyclopentadienyl complex decreases, arises as a weak shoulder in the case of **1**, **2**, and **5**. No splitting of the E mode[7] was observed. The absence of the B_1 band in most of the complexes $Cp'V(CO)_4$ shows that the effective local symmetry is still C_{4v}; i.e. there are no rotational barriers for Cp′ at room temperature. Compelxes **1**, **4**, and **5** have also been characterized by their mass spectra,[8] showing a frag-

---

(1) Kowalewski, R. M.; Kipp, D. O.; Stauffer, K. J.; Swepston, P. N.; Basolo, F. *Inorg. Chem.* **1985**, *24*, 3750.

(2) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *131*, 273.

(3) Wenke, D.; Rehder, D. *J. Organomet. Chem.* **1984**, *273*, C43.

(4) Hoch, M.; Rehder, D. *J. Organomet. Chem.* **1985**, *288*, C25.

(5) $n^{18.5}{}_D$ 1.4702; melting range 10–14 °C.

(6) Hartmann, H.; Flenner, K.-H. *Z. Phys. Chem.* (*Liepzig*) **1950**, *194*, 278.

(7) Palyi, G.; King, R. B. *Inorg. Chim. Acta* **1975**, *15*, L23.

(8) Selected peaks, *m/e* (relative intensities in parentheses), are as follows: (indenyl)$V(CO)_4$: 278 (7), $C_9H_7V(CO)_4$; 250 (10), $C_9H_7V(CO)_3$; 222 (12), $C_9H_7V(CO)_2$; 194 (10), $C_9H_7V(CO)$; 166 (100), C_9H_7V; 140 (11), C_7H_5V; 115 (24), C_9H_7; 89 (7), C_7H_5; 76 (7), C_6H_4; 65 (15), C_5H_5. {(Et)Me_4C_5}$V(CO)_4$: 312 (52), (Et)$Me_4CpV(CO)_4$; 284 (46), (Et)-Me_4(Cp$V(CO)_3$; 256 (31), (Et)$Me_4CpV(CO)_2$; 228 (68), (Et)-$Me_4CpV(CO)$; 200 (100), (Et)Me_4CpV; 185 (45), possibly η-$C_6Me_5H_2V$; 184 (90), likely corresponding to {η^6-C_6Me_5H}V, a plausible fragment of $[(\eta^6\text{-arene})V(CO)_4]^+$ (Calderazzo, F.; Pampaloni, G.; Vitale, D.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1982**, 1993)); 51 (65), V; metastable peaks 175.4 ($EtMe_4CpV(CO)^{\bullet+} \rightarrow EtMe_4CpV^{\bullet+} + CO$), 169.3 ($EtMe_4CpV^{\bullet+} \rightarrow C_6Me_5HV^{\bullet+} + CH_4$). {Me(cetyl)$H_3C_5$}$V(CO)_4$: 466 (2), Me(cetyl)Cp$V(CO)_4$; 438 (1), Me(cetyl)-Cp$V(CO)_3$; 410 (1), Me(cetyl)$V(CO)_2$; 382 (2), Me(cetyl)$V(CO)$; 354 (43), Me(cetyl)V; 303 (100), Me(cetyl)Cp; 70 (7), C_5H_{10}; 56 (41), C_4H_8; 42 (79), C_3H_4. The following peaks correspond to the fragmentation pattern of the cetyl fragment c-{C_3(Me)H}$(CH_2)_nCH_3$ (*n* and the relative intensities are given in parentheses): 178 (*n* = 9; 2), 164 (*n* = 8; 6), 150 (*n* = 7; 7), 136 (*n* = 6; 16), 122 (*n* = 5; 23), 108 (*n* = 4; 77), 94 (*n* = 3; 80).

Table II. Spectroscopic Data for η^5-Cp′V(CO)$_4$ Complexes

complex	Cp′[a]	$\delta(^{51}V)$[b]	$W_{1/2}$[c]	ν(CO),[d] cm^{-1}			
1	indenyl	+159	50	2037 m	1950 w	1929 vs	
2	C_5(trityl)H_4	+50	345	2030 m	1945 w	1925 vs	1888 sh[e]
3	C_5Me_5	+44	25	2023 m		1913 vs	1885 sh[e]
4	C_5(Et)Me_4	+31	50	2024 m		1914 vs	1885 w[e]
	$C_5(CHPh_2)H_4$[f]	+27		2015		1910	
5	C_5Me(cetyl)H_3[g]	+19.1, +16.0	60	2034 m	1942 sh	1921 vs	1893 sh[e]
6	C_5Me(Cy)H_3[g]	+18.9, +16.6	45	2022 m		1920 vs	1895 sh[e]
7	C_5MeH_4	+9.1	45	2038 m		1927 vs	1898 sh[e]
	C_5H_5	0	20	2030 m[h]		1933 vs	1902 vw[e]

[a] For abbreviations see Table I. [b] In hexane solution relative to η^5-$C_5H_5V(CO)_4$. The shift of the latter relative to $VOCl_3$, the standard adopted in ^{51}V NMR spectroscopy, is −1534 ppm.[4,12,13] The spectra were obtained on a Bruker AM 360 spectrometer at 94.55 MHz (acquisition time 0.041 s, pulse width 10 μs) with a resolution of 12 Hz/point (0.12 ppm). [c] Width of the resonance signal at half-height in Hz. [d] Hexane solution, in 0.1-mm KBr cuvettes. [e] Probably the ^{13}C satellite. [f] From ref 3 (in toluene solution). [g] Two geometrical isomers (with the substituents in 1,2- and 1,3-positions, respectively) in almost equal amounts. For assignment see Figure 1. [h] IR data from ref 7.

mentation pattern very much reminiscent of $C_5H_5V(CO)_4$.[9]

The complexes have been obtained by refluxing $V(CO)_6$ and a 20% excess of HCp′ in *n*-hexane, avoiding exposure to direct sunlight. In a side reaction competitive with eq 1, small amounts of $[Cp'_2V(CO)_2][V(CO)_6]$ (eq 2) are also formed. The ionic

$$2V(CO)_6 + 2HCp' \rightarrow [Cp'_2V(CO)_2][V(CO)_6] + 4CO\ (+H_2) \tag{2}$$

complex, which for Cp′ = C_5Me_5 has been synthesized formerly from $V(CO)_6$, Cp'_2V, and CO[10] or from $Cp'_2V(\mu\text{-}CO)V(CO)_5$,[11] precipitates together with finely divided vanadium metal and can be separated by extraction with $CHCl_3$. Lower reaction temperatures (coupled with longer reaction times) increase the yield of $[Cp'V(CO)_2][V(CO)_6]$ at the expense of $Cp'V(CO)_4$. The complexes $Cp'V(CO)_4$ are light-sensitive, especially the cyclohexyl derivative **6**.

The methylalkylcyclopentadienes have been prepared as indicated by eq 3. Because of their tendency to dimerize and

$$(C_5MeH_5)_2 \rightarrow C_5MeH_5 \xrightarrow{\text{NaH (THF)}} NaC_5MeH_4 \xrightarrow{\text{RBr (THF)}} C_5Me(R)H_4 \tag{3}$$

oligomerize (only C_5Me(cetyl)H_4 and C_5(trityl)H_5 are stable as monomers), they were reacted immediately after preparation. As evidence indirectly by the ^{51}V NMR spectra of the complexes $Cp'V(CO)_4$, C_5Me(Cy)H_4 and C_5Me(cetyl)H_4 are obtained as an almost equimolar amount of the 1,2- and 1,3-isomers.

The ^{51}V chemical shift range for the cyclopentadienyl complexes (−1375 to −1534 ppm relative to $VOCl_3$)[12] compares to the δ values for other half-sandwich complexes such as η^7-TpV(CO)$_3$ (−1485 ppm; Tp = tropylium) and $[\eta^6\text{-TolV(CO)}_4]^+$ (−1660 ppm; Tol = toluene) and to those for phosphine-stabilized (η^3-allyl)V(CO)$_5$ (−1355 to −1445 ppm[13]). There is a distinct dependence of the shielding of the ^{51}V nucleus upon the nature of the substituents on the Cp ring (Figure 1). Deshielding effects induced by substituent effects primarily electronic in nature (viz. by a decrease of the electron density in the aromatic system) and/or primarily of steric origin (increase of the bulk of the substituent) have been reported, inter alia, for the ^{51}V NMR shifts of V(η^2-COR)(CO)$_3$(PP) (PP = bis(phosphine); R = substituted phenyl),[14] the ^{95}Mo NMR shifts of (η^6-aryl)Mo(CO)$_3$,[15] and the ^{49}Ti NMR shifts of $(\eta^5\text{-}C_5R_5)_2TiX_2$ (X = F, Cl, Br; R = H, Me).[16] The especially electron-poor η^5-indenyl system gives rise to a large downfield shift (i.e. deshielding of the ^{51}V nucleus) with respect to $C_5H_5V(CO)_4$, similar to that observed in η^3-allyl complexes (vide supra). Disregarding steric influences, an opposite trend should arise for alkyl-substituted cyclopentadienyls. However (cf. Table II), this is not the case. Steric crowding at the ligand will give rise to a weakening of the interaction between the metal and the aromatic system[15] and hence to a secondary electronic effect pointing into the opposite direction (deshielding of the ^{51}V nucleus[12]) and apparently overriding primary electronic effects. The increase of ^{51}V shielding in the order **1**, **2**, **3**, **4**, $C_5(CHPh_2)H_4V(CO)_4$, **5**, **6**, **7**, $C_5H_5V(CO)_4$ hence reflects decreasing steric requirement of Cp′.

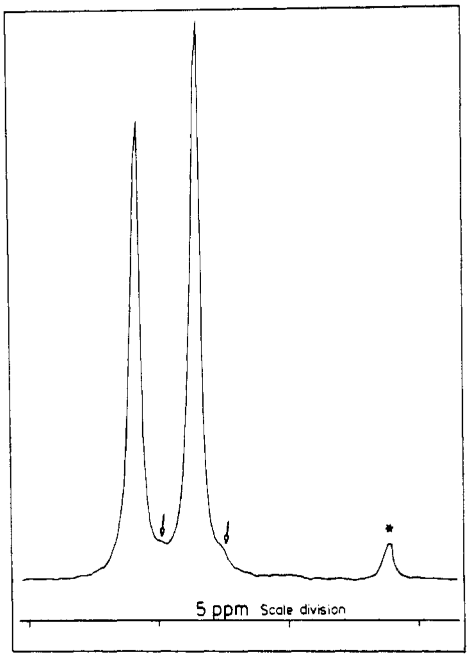


Figure 1. 94.55-MHz $^{51}V\{^1H\}$ NMR spectrum of η^5-{C_5Me(Cy)H_3}V(CO)$_4$ (**6**). The low-field (high-frequency) signal likely is the 1,2-isomer, and the high-field signal, the 1,3-isomer (intensity ratio 4/5). These assignments are based on the assumption that the 1,2-isomer is the sterically more hindered one and thus should exhibit a downfield shift relative to the 1,3-isomer (cf. the text for the discussion of steric effects). Shoulders (indicated by arrows) correspond to the high-field component of the doublet for the naturally abundant ^{13}C satellite, for which an isotope shift of −0.45 ppm is anticipated.[17] The small signal to the right (*) is an impurity of η^5-$C_5MeH_4V(CO)_4$ (**7**).

Since the ^{51}V nucleus (nuclear spin $^7/_2$) has a quadrupole moment, relaxation times are governed by the quadrupole relaxation mechanism. Bulky substituents on the Cp ring should then give rise to broad resonance signals due to a decrease of molecular motion. An increase of the line width $W_{1/2}$ by the factor of 2 is indeed observed for complexes **1** and **4**–**7** with respect to $C_5H_5V(CO)_4$ (20 Hz, Table II). The most drastic increase of $W_{1/2}$ has been noted for trityl complex **2** (345 Hz) which, in the series

---

(9) King, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 1412.
(10) Calderazzo, F.; Bacciarelli, S. *Inorg. Chem.* **1963**, *2*, 721.
(11) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 6292.
(12) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.
(13) Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33.
(14) Schiemann, J.; Weiss, E. *J. Organomet. Chem.* **1983**, *255*, 179.
(15) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1981**, *20*, 4183.
(16) Gassman, P. G.; Champbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385.
(17) Hoch, M.; Rehder, D. *Inorg. Chim. Acta* **1986**, *111*, L13.

Inorg. Chem. **1986**, *25*, 2909–2910 **2909**

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.

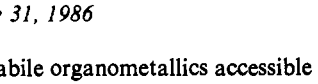
Contribution from Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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

John Godber, Helmut X. Huber, and Geoffrey A. Ozin*

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]



$$\mathrm{Ni} + \mathrm{N_2} \begin{cases} \xrightarrow{77\ \mathrm{K}} \mathrm{Ni}_x(\mathrm{N_2})_{\mathrm{chemisorbed}} \\ \xrightarrow{12\ \mathrm{K}} \mathrm{Ni(N_2)_4} \end{cases}$$

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.

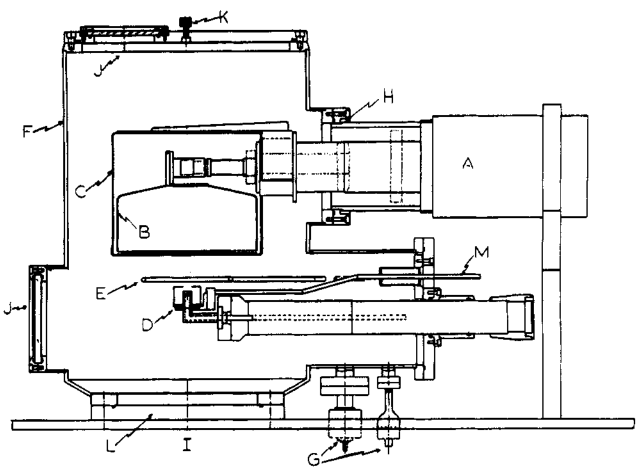


Figure 1. Preparative-scale matrix isolation equipment for conducting metal vapor synthesis over the extended temperature range 15–300 K. Figure notation: (A) high-refrigeration-capacity cryopump (Air Products); (B) reaction cryoshield on first stage (4 W at 10 K); (C) radiation shield on 77 K second 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-

---

(1) Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118 and references cited therein.
(2) Skell, P. S.; Havel, J. J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97 and references cited therein.
(3) Ozin, G. A., Moskovits, M., Eds. *Cryochemistry*; Wiley: New York, 1976. Ozin, G. A. *CHEMTECH* **1985**, 488. Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer Verlag: New York, 1979. Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980, and references cited therein.
(4) Hallam, H. E., Ed. *Vibrational Spectroscopy of Trapped Species*; Wiley: New York, 1973, and references cited therein.
(5) Huber, H. X.; Kundig, E. P.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 332. Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273.
(6) Kundig, E. P. Ph.D. Thesis, University of Toronto, 1975.