Inorganica Chimica Acta, *83* (1984) 137–141

Preparation of Tris(η^5-cyclopentadienylcobaltmonocarbonyl) Cluster Complex by a Plasma Technique

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Received June 14, 1983

The glow discharge reaction of cyclopentadienyldicarbonylcobalt(I) $CpCo(CO)_2$ was carried out in an inductively coupled cylindrical reactor at various flow rates and rf power levels. The deposition rate at low ratios of power to flow rate (W/F) is highest near the monomer inlet; a relatively uniform deposition rate distribution is observed at higher values of W/F. This suggests a plasma reaction of relatively rapid kinetics occurring at low W/F but not at higher W/F. The product of this reaction deposited at the monomer inlet was analyzed by infrared and ^{1}H-nmr spectroscopy and was found to include the cluster complex tris(η^5-cyclopentadienylcobaltmonocarbonyl), $[CpCo(CO)]_3$. The maximum yield of $[CpCo(CO)]_3$ was obtained at the lowest W/F attainable with our reactor.

Introduction

The field of plasma chemistry includes several disciplines, each related to the preparation of a specific type of product, including organic plasma synthesis (for the preparation of organic and organometallic compounds) [1–4], plasma polymerization (the formation of highly crosslinked amorphous, organic polymer thin film coatings) [5] and the plasma preparation of inorganic thin films [6] (*e.g.*, silicon nitride and hydrogenated amorphous silicon [7]) [8].

In the course of a research program dealing with the preparation and characterization of transition metal containing plasma polymers, we have found that a portion of the involatile product formed on exposing the vapor of η^5-cyclopentadienyldicarbonylcobalt(I), $CpCo(CO)_2$, to a plasma is the cluster complex tris(η^5-cyclopentadienylcobaltmonocarbonyl), $[CpCo(CO)]_3$. The synthesis of this compound has been reported previously [9–12] by photolysis of $CpCo(CO)_2$ in an appropriate solvent. Reports have also been made concerning the related dimer and tetramer clusters $Cp_2Co_2(CO)_3$ and $Cp_4Co_4(CO)_2$ and their mechanisms of interconversion in solution [10–12]. Cotton *et al.*, [13, 14] reported the structure of the trimer $[CpCoCO]_3$ to contain a triply bridging CO in addition to two semibridging CO ligands. Our results are of interest because they delineate a transition between two of the disciplines arbitrarily defined above (organic plasma synthesis and plasma polymerization), because they can easily be extrapolated to a practical plasma method for the synthesis of $[CpCo(CO)]_3$ and similar cluster compounds, and because they suggest methods of forming novel transition metal containing plasma polymers (*e.g.*, with cluster complexes bonded to the 'main chain') [15].

Experimental

η^5-Cyclopentadienyldicarbonylcobalt(I) (Aldrich Chemical Co. and Strem Chemical Co.) was stored *in vacuo* in the dark at –76 °C, and warmed to 24 °C during glow discharge synthesis. The monomer was used as received in early work and later, after purification by trap-to-trap distillation.

Glow discharge reactions were carried out in the inductively coupled reactor previously described [16] and illustrated schematically in Fig. 1. $CpCo(CO)_2$ monomer was fed into the reactor vessel through an orifice of 2 mm diameter. Pressure was measured using a MKS differential pressure transducer. The transducer was also used to obtain flow rates by measurements of the increase in pressure with time as monomer is fed into a closed system (no pump-out) of known volume. An electrodeless radiofrequency discharge (13.56 MHz) was used to initiate

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0020-1693/84/$3.00

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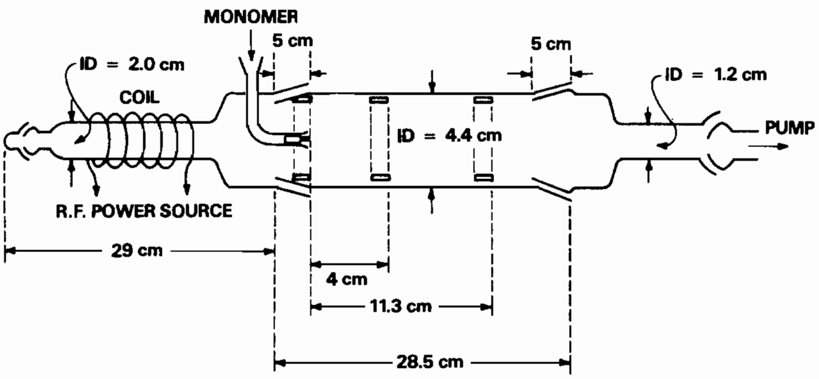

Fig. 1. Schematic representation of plasma reaction chamber showing location of aluminum foil strips fitted circumferentially in the reactor to collect plasma polymer for the spectra shown in Fig. 4.

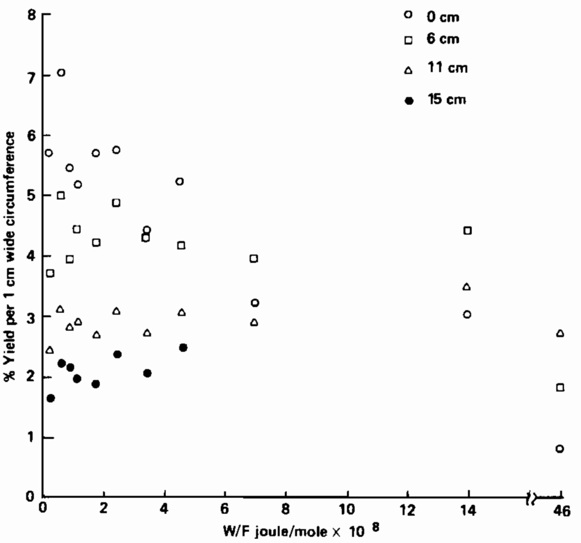

Fig. 2. Plot of deposition rate *versus* W/F for $CpCo(CO)_2$ plasma discharge reaction. The deposition rate (expressed as weight % yield per 1 cm wide circumference) was obtained at 4 locations within the reactor. Plasma discharges were carried out by keeping power at 50 W and varying flow rate or using a constant flow rate (0.28 cm^3/mm) and varying power. The pressure prior to initiating glow discharge (P_m) was generally 20 mtorr.

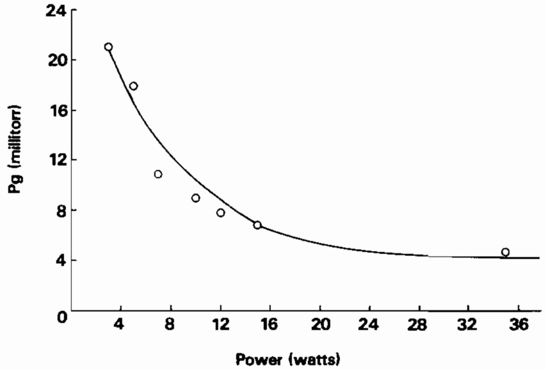

Fig. 3. Variation of Pg [plasma pressure inside the reactor during glow discharge of $CpCo(CO)_2$] *versus* power (watts) at constant flow rate (F = 0.26 cm^3/mm) and Pm (8 mtorr).

the plasma maintaining the reflected power at the minimum.

The deposition rate of the products was calculated from the weight gain of the glass cover slips (2.2 X 2.2 cm). Infrared spectra were taken using the attenuated total reflection (ATR) technique with a Nicolet 7199 Fourier transform infrared spectrometer (FTIR). The plasma products were deposited on aluminum foil which was pressed against a 45° KRS-5 internal reflection element. Certain infrared spectra were also measured by transmission through products deposited on the surface of NaCl crystals. ^{1}H-nmr spectra were obtained from sealed samples protected from room light using a Bruker WM-250 250 MHz spectrometer.

Results and Discussion

The glow discharge polymerization of $CpCo(CO)_2$ was studied over a range of power to flow rate ratios. Deposition rates are plotted *versus* W/F in Fig. 2 for three (sometimes four) locations within the reactor. It was observed that for a low W/F plasma, there is a pronounced prevalence of deposition close to the monomer inlet. However, at intermediate values of W/F (7–14 X 10^8 Joules/mol) the highest deposition rate is obtained at a site 6 cm from the monomer inlet, while at the highest power to flow

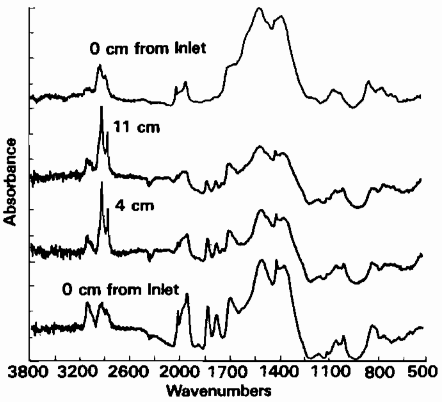

Fig. 4. Three infrared spectra of $CpCo(CO)_2$ plasma polymer deposited at various sites within the reactor at low W/F and one spectrum for high W/F plasma polymer. Glow discharge conditions for the bottom three spectra were $W/F = 0.25 \times 10^8$ Joules/mol, $F = 0.27$ cm^3 (STP)/min, power = 5 watts, and Pg = 19.6 mtorr. The top infrared spectrum is for Cp-$Co(CO)_2$ plasma polymer deposited under monomer inlet under the following plasma conditions: $W/F = 1.72 \times 10^8$ Joules/mol, $F = 0.39$ cm^3/min, power = 50 watts, Pg = 7.8 mtorr, vacuum valve closed.

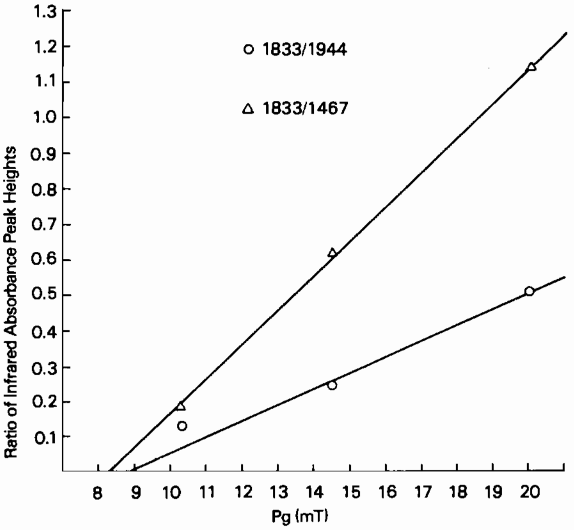

Fig. 5. Plot of ratio of bridging carbonyl infared peak height (1833 cm^{-1})/terminal carbonyl infrared peak height (1944 cm^{-1}) and bridging carbonyl infrared peak height (1833 cm^{-1})/plasma polymer infrared peak height (1467 cm^{-1}) as a function of Pg (mtorr) for various glow discharge reactions of $CpCo(CO)_2$. Flow rate was maintained constant ($F = 0.21$ cm^3/min.

rate ratio the site of highest deposition rate is that furthest removed from the monomer inlet.

Pg (plasma pressure inside the reactor in a glow discharge of $CpCo(CO)_2$) was also found to vary with W/F. This is shown in Fig. 3 where Pg is plotted *versus* W (power) at constant flow rate (0.26 cm^3/min) and Pm (pressure inside reactor prior to initiation of glow discharge = 8 mtorr). From Fig. 3 it is clear that at low power, Pg is a very sensitive function of power. In contrast, at higher power, Pg decreased only from 4.6 to 4 mtorr with an increase in power from 35 to 70 watts.

The sensitivity of deposition rate distribution and Pg to W/F for $W/F < 0.40 \times 10^8$ Joules/mol, suggests that the product formed below $W/F = 0.40 \times 10^8$ Joules/mol differs chemically from that formed at higher values of W/F. That this is so can be demonstrated by infrared spectra taken for plasma deposit formed above and below $W/F = 0.25 \times 10^8$ Joules/mol. Such spectra are shown in Fig. 4. It is clear that peaks at 1693, 1777, 1832, and 3100 cm^{-1} are present when the product is formed at the lower W/F but not at the higher. Spectra taken at $W/F = 0.25 \times 10^8$ Joules/mol for product formed at various locations within the reactor show that these peaks are most prominent for the product deposited directly under the monomer inlet. The peak at 3100 cm^{-1} is assigned to the cyclopentadienyl C—H stretch while the peaks at 1776 and 1832 cm^{-1} coincide with the peaks observed for $[CpCoCO]_3$ in the solid state, indicative of bridging carbonys [13, 14]. An additional peak is present in the infrared spectrum of trimer at 1673 cm^{-1} and ascribed to a triply bridging carbonyl [13, 14]. A broad peak is present in the spectrum of the plasma deposited product whose shoulder includes 1673 cm^{-1}, but which is most intense at 1693 cm^{-1}. However exact correspondence with the infrared spectrum of the trimeric cluster compound can be achieved by careful control of the plasma reaction conditions and purity of the monomer vapor, as will be shown below. The data presented above suggest that slightly rearranged product is deposited close to the monomer inlet at low W/F, while products from extensive decomposition of the monomer are deposited more evenly over the reactor. At higher W/F, only products of extensive decompositon are deposited throughout the reactor.

As a measure of the relative amount of the trimeric cluster in a given plasma product, we used the peak height ratios of the 1833 cm^{-1} peak to the 1944 and 1467 cm^{-1} peaks respectively. These peak height ratios are plotted as a function of Pg in Fig. 5. These experiments were run at a flow rate of 0.21 cm^3/min. Pg was controlled by variation in rf power, *i.e.*, Pg was increased by decreasing rf power (see Fig. 3). It is seen that the yield of the trimeric cluster compound increases as both Pg and deposition rate nonuniformity increase. This suggests that at low W/F, the $CpCo(CO)_2$ molecules in the plasma state release CO ligands to form the trimeric cluster. At higher W/F incorporation of CO in the

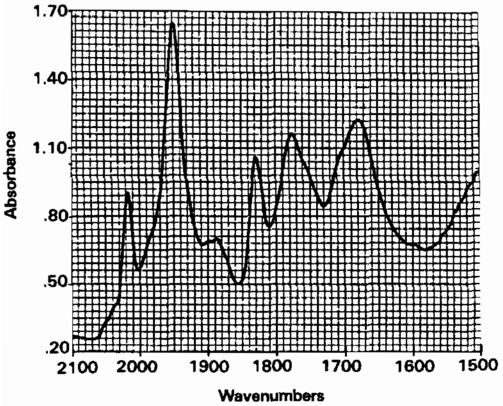

Fig. 6. Expanded version of CO stretch portion of infrared spectrum when glow discharge of $CpCo(CO)_2$ was carried out at Pg = 20 mtorr, F = 0.245 cm^3/min, and power = 3.75 watts.

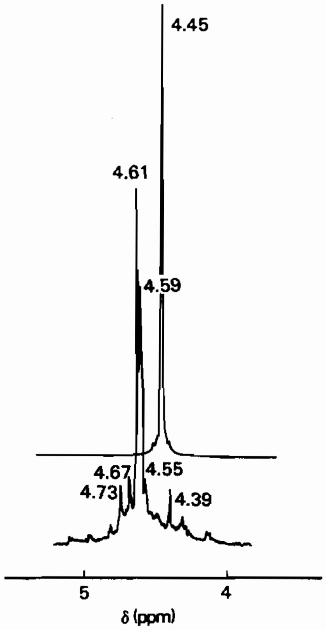

Fig. 7. Proton nmr spectra of $CpCo(CO)_2$ monomer (top) and glow discharge product of $CpCo(CO)_2$ near monomer inlet (using the conditions of Fig. 6) in benzene-d_6 (bottom).

plasma polymer as an aldehydic or ketonic CO group occurs causing a peak at ~1700 cm^{-1} which overlaps the trimeric cluster peak at 1673 cm^{-1}. Decomposition of any trimer formed also occurs at higher W/F.

The solubility of the product yielding the infrared peaks at 1833 and 1775 cm^{-1} in tetrahydrofuran (THF), a known solvent for the trimeric cluster compound, was demonstrated as follows. Plasma product was deposited on Al foil at Pg = 14.5 mTorr. The IR spectrum of the coating indicated IR peaks at 1833 and 1755 cm^{-1} at less than maximum yield (See Fig. 5). The product was extracted with distilled THF solvent (resulting in a 3% weight loss for the coating) and the IR spectrum was obtained again using the same Al foil, for which visual inspection showed no alteration of the coating. It was observed that bridging carbonyl peaks had been eliminated. Thus the product containing bridging carbonyl is partially soluble in THF as would be expected if said product contained $[CpCo(CO)]_3$.

By careful control of plasma reaction conditions and monomer purity, a maximum yield of product whose infrared and nmr spectra corresponded exactly to that of the trimeric cluster compound was obtained. The purity of the $CpCo(CO)_2$ monomer was established by nmr, condensing the vapors of $CpCo(CO)_2$ in benzene-d_6 in an nmr tube at −196 °C. A sharp singlet resonance at δ 4.45 (Fig. 7) due to 5 equivalent η^5-cyclopentadienyl protons, in good agreement with that observed by Vollhardt *et al.* [10] for $CpCo(CO)_2$ in benzene-d_6 is the only prominent feature of the spectrum.

The conditions for deposition of maximum yield of the trimer tris(η^5-cyclopentadienylcobaltmonocarbonyl) near the monomer inlet were as follows: Pg = 20 mtorr, F = 0.245 cm^3/min at S.T.P. and power approximately 4 watts. Using these conditions $[CpCoCO]_3$ (and plasma polymer) was deposited on a strip of aluminum foil (7 X 3 cm) placed around the circumference of the reactor at the monomer inlet. Such a deposit yielded an infrared spectrum with bridging carbonyl peaks at 1674, 1775 and 1830 cm^{-1} as shown in Fig. 6. This is in excellent agreement with the reported spectrum for tris(η^5-cyclopentadienylcobaltmonocarbonyl), $[CpCoCO]_3$ [13, 14]. This trimer was extracted with THF* stripped, and the residue redissolved in benzene-d_6. A ^{1}H-nmr spectrum of this solution is hown in Fig. 7. The intense signals observed at δ 4.59 and δ 4.61 correspond to that reported by Vollhardt *et al.*, [10] for $[CpCoCO]_3$ and $Cp_2Co_2(CO)_3$, respectively. The signal obtained for the parent compound $CpCo(CO)_2$ is included in Fig. 7 as a reference point.

Conclusions

Plasma polymerization of $CpCo(CO)_2$ formed $[CpCo(CO)]_3$ in an inductively coupled cylindrical reactor as indicated by the IR spectrum of the

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*Trimer yield could not be determined by weight loss as described above for non-maximum trimer yield) because the coating obtained at the conditions of maximum trimer yield disintegrates on exposure to THF solvent.

plasma polymer and the nmr spectrum of THF soluble material extracted from the plasma polymer. It is observed that the $[CpCo(CO)]_3$ is deposited preferentially under the monomer inlet and at low W/F. To our knowledge this is the first report of the preparation of a transition metal cluster compound via a plasma technique.

Acknowledgment

This work was made possible by NSF Grant Number CPE-8006805.

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