Electroactive Metal Clusters as Models of Electrode Surfaces: Vibrational Spectroelectrochemistry of Seven Redox Forms of $[Pt_{24}(CO)_{30}]^n$ (n = 0 to −6) and Comparison with Potential-Dependent Spectra of CO Chemisorbed on Platinum

Gregory J. Lewis,[1] Joseph D. Roth,[2] Ruth A. Montag,[1]
Lance K. Safford,[2] Xiaoping Gao,[2] Si-Chung Chang,[2]
Lawrence F. Dahl,*[1] and Michael J. Weaver*[2]

Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received November 15, 1989

Herein are reported sequences of vibrational spectra in the C–O stretching (ν_{CO}) region for seven resolvable redox forms of the platinum carbonyl cluster, $[Pt_{24}(CO)_{30}]^n$ (n = 0 to −6) in dichloromethane. These were obtained by means of real-time FTIR spectroscopy during thin-layer cyclic voltammetry of $[Pt_{24}(CO)_{30}]^{2-}$.[3-5] Comparison with infrared spectra for CO adsorbed on a platinum electrode in dichloromethane enables a direct correlation to be made of the potential-dependent vibrational behavior of CO coordinated to the cubic close-packed (ccp) Pt_{24} core with CO electrochemisorbed to a polycrystalline (ccp) Pt electrode. The present results illustrate the tremendous potential of vibrational spectroelectrochemistry for probing the redox-dependent spectral behavior of high-nuclearity metal clusters.

Figure 1 includes a typical cyclic voltammogram (0.1 V s^{-1}) with solution resistance (*iR*) compensation for ca. 4.5 mM $[AsPh_4]_2[Pt_{24}(CO)_{30}]$ in dichloromethane, containing 0.15 M $[NBu_4]^+[ClO_4]^-$ as supporting electrolyte.[5] Six redox couples are discernable; four reversible voltammetric waves are observed at potentials negative of the open-circuit value, ca. 0 V vs aqueous Ag/AgCl, with a further two reversible waves[6] situated at more positive potentials. The cathodic–anodic peak separation in most cases approaches 60–70 mV with *iR* compensation, especially at low scan rates (≤0.5 V s^{-1}) which, together with the comparable amplitudes of all waves, are consistent with the occurrence of one-electron steps. We therefore conclude that the six redox couples comprise seven distinct $[Pt_{24}(CO)_{30}]^n$ forms (n = 0 to −6), with formal potential (E_f) values as follows (vs Ag/AgCl): 0.69 V (0/1−), 0.44 V (1−/2−), −0.38 V (2−/3−), −0.64 V (3−/4−), −1.13 V (4−/5−), and −1.39 V (5−/6−) (±0.01 V).

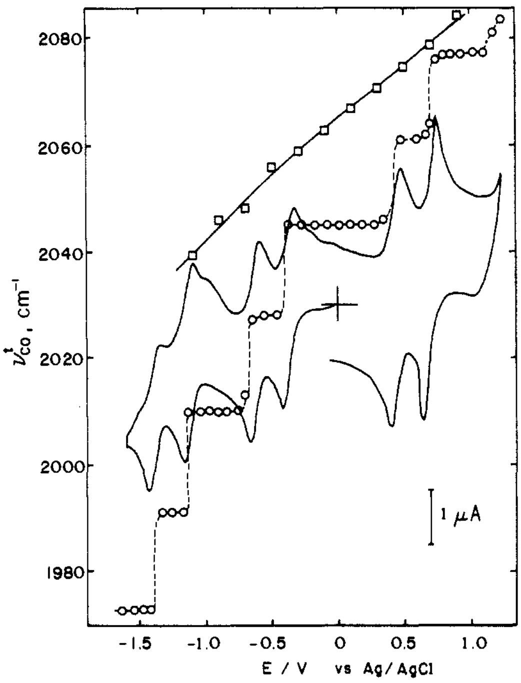

Figure 1. Infrared frequency of terminal carbonyl band, ν_{CO}^t, for $[Pt_{24}(CO)_{30}]^n$ (n = 0 to −6) in dichloromethane (circles, dashed trace) as a function of electrode potential, *E*. Superimposed is a cyclic voltammogram of 4.5 mM $[Pt_{24}(CO)_{30}]^{2-}$ on the same potential scale. Sweep rates for infrared and electrochemical measurements were 5 and 100 mV s^{-1}, respectively. These experiments employed a large (0.9-cm diameter) gold disk and a platinum bead (area 2.0 × 10^{-3} cm^2), respectively. Also shown (squares, solid line) is a ν_{CO}^t vs *E* plot for a CO monolayer on a polycrystalline Pt electrodes in dichloromethane obtained by surface infrared spectroscopy under comparable conditions.[13]

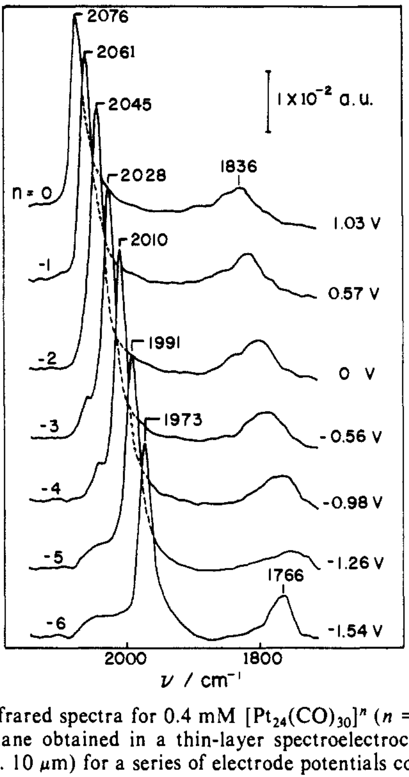

Figure 2. Infrared spectra for 0.4 mM $[Pt_{24}(CO)_{30}]^n$ (n = 0 to −6) in dichloromethane obtained in a thin-layer spectroelectrochemical cell (thickness ca. 10 μm) for a series of electrode potentials corresponding to the redox states (n) indicated. Each spectrum involved acquiring five interferometer scans during a slow (5 mV s^{-1}) potential sweep, a prior solvent "blank" spectrum being subtracted in each case.

Figure 2 shows a set of infrared spectra in the ν_{CO} frequency region obtained for the same seven species (n = 0 to −6) during a similar cyclic voltammogram, but at 5 mV s^{-1} in a thin-layer spectroelectrochemical cell.[7,8] The FTIR spectrometer was an IBM (Bruker) IR 98-4A vacuum instrument, with a Globar light source and a MCT narrow-band detector.[9] Each spectrum was

---

(1) University of Wisconsin—Madison.

(2) Purdue University.

(3) For relevant material on high-nuclearity platinum carbonyl clusters, see: (a) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (b) Lauher, J. W. *J. Organomet. Chem.* **1981**, *213*, 25. (c) Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* **1984**, *55*, 151. (d) Teo, B. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1362. (e) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1352. (f) Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968. (g) Mingos, D. M. P. *Chem. Soc. Rev.* **1986**, *15*, 31. (h) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123. (i) Teo, B. K.; Sloane, N. J. A. *Inorg. Chem.* **1985**, *24*, 4545. (j) Mingos, D. M. P.; Zhenyang, L. *J. Chem. Soc., Dalton Trans.* **1988**, 1657. (k) Wales, D. J.; Stone, A. J. *Inorg. Chem.* **1989**, *28*, 3120. (l) Kharas, K. C. C.; Dahl, L. F. *Adv. Chem. Phys.* Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1988; Vol. 70, Part 2, p 1.

(4) Montag, R. A.; Ceriotti, A.; Dahl, L. F., submitted for publication.

(5) The brown $[Pt_{24}(CO)_{22}(\mu_2\text{-}CO)_8]^{2-}$ dianion was obtained from thermolysis of the $[Pt_{15}(CO)_{30}]^{2-}$ dianion in THF.[4] Its idealized C_{2v} structure, established[4] from single-crystal X-ray diffraction studies, possesses a wedge-shape Pt_{24} core with one encapsulated and 23 surface Pt atoms and two mirror-related 10-atom Pt(111) faces.

(6) The most positive (0/1−) redox wave is apparently complicated by some cluster deposition on the electrode surface.

(7) The spectroelectrochemical cell was of the thin-layer-reflectance type, with a retractable gold disk electrode and a CaF_2 optical window. Solutions can be injected and flushed through via a small entry port in the optical window.[8]

(8) Roth, J. D.; Weaver, M. J., to be published.

acquired by using five interferometer scans (consuming ca. 3 s). The seven spectra in Figure 2, selected from this sequence, refer to potentials (as indicated) where each of the seven redox states is almost exclusively present. Each spectrum displays an intense potential-dependent terminal carbonyl band (ν_{CO}^{t}), at 2076 cm^{-1} for $n = 0$ and 1973 cm^{-1} for $n = -6$, and a weaker doubly bridging carbonyl band (ν_{CO}^{b}) centered at 1836 cm^{-1} for $n = 0$ and 1766 cm^{-1} for $n = -6$. The relative intensities of these features are consistent with the 22 terminal and eight bridging carbonyls present in the solid-state structure of $[Pt_{24}(CO)_{30}]^{2-}$,[5] indicating that the overall cluster configuration is maintained for all seven redox forms.

Figure 2 shows that sequential one-electron reduction of the $[Pt_{24}(CO)_{30}]^{n}$ species results in near-uniform decreases in ν_{CO}^{t} and ν_{CO}^{b}; the ν_{CO}^{t} downshift is 15 cm^{-1} for $[Pt_{24}(CO)_{30}]^{0/1-}$ increasing to 19 cm^{-1} for $[Pt_{24}(CO)_{30}]^{5-/6-}$. The ν_{CO}^{t} vs potential dependence is also included (circles, dashed trace) in Figure 1. Sharp reversible alterations in ν_{CO}^{t} occur within narrow (40–50 mV) potential regions that match consistently to the voltammetric E_f values. This confirms that the infrared spectral shifts correspond to the same redox transformations observed by cyclic voltammetry. Corresponding Raman spectroelectrochemical measurements were also undertaken in order to examine the redox-induced changes in the Pt–C stretch, ν_{PtC}, region. Although relatively concentrated ($\gtrsim$5 mM) $[Pt_{24}CO_{30}]^{2-}$ solutions were required to obtain reliable spectra (514.5-nm laser excitation), ν_{PtC} was observed to increase with increasingly negative n (e.g., ca. 450 cm^{-1} for $n = -2$, 480 cm^{-1} for $n = -6$).

These results provide an unprecedented opportunity to examine the sensitivity of the carbonyl bonding to the "surface charge density" of a high-nuclearity metal cluster. The almost linear decrease of ν_{CO}^{t} observed as n becomes more negative is not surprising in that the extent of $d\pi(Pt) \rightarrow \pi^*(CO)$ backbonding should be related directly to the overall negative charge of the Pt_{24} core (the "charge effect").[10] A plot of ν_{CO}^{t} versus the excess electronic charge per *surface* Pt atom has a slope of 405 cm^{-1}/e; interestingly, the observed ν_{CO}^{t} values for the hcp $[Pt_{26}(CO)_{32}]^{2-}$ and ccp $[Pt_{38}(CO)_{44}]^{2-}$ dianions (2042 and 2052 cm^{-1}, respectively[11]) fall on the same line.

Such charge-induced ν_{CO} frequency shifts are entirely analogous to the potential-induced ν_{CO} shifts for CO chemisorbed to metal electrodes.[12] Figure 1 also includes a plot (solid line) of ν_{CO}^{t} versus electrode potential, E, obtained for an irreversibly adsorbed CO monolayer on polycrystalline platinum in the same dichloromethane medium.[13] (These results were obtained by surface FTIR as described in ref 9.) Intriguingly, the Pt surface and cluster systems display similar ν_{CO}^{t} vs E behavior. Of course, the "discrete" ν_{CO}^{t} vs E dependence for the cluster reflects in part its microscopic dimensions. The spacings between adjacent E_f values alternate between small (ca. 0.25 V, $n = -1, -3, -5$) and larger values (ca. 0.5–0.8 V; $n = -2, -4$), suggesting that the added electrons enter successive LUMOs in a pairwise fashion.[14] The average ν_{CO}^{t} vs E slope for the cluster, ca. 30–40 cm^{-1} V^{-1}, is somewhat larger than for the electrode case, 20 cm^{-1} V^{-1}. This difference possibly reflects the influence of ionic solvation, which will shift the E_f values increasingly in the positive direction as the cluster charge increases. As expected on this basis, the ν_{CO}^{t} values in the surface and cluster environments are closest at potentials (>0.7 V) where the latter is uncharged. Quantitative comparison with ν_{CO}^{t} for an uncharged Pt electrode is hampered by a lack of reliable potential of zero charge values.[15] Nevertheless, ν_{CO}^{t} for a saturated CO layer on Pt(111) in ultrahigh vacuum at 300 K (2095 cm^{-1})[16] is significantly higher than for the neutral cluster $Pt_{24}(CO)_{30}$ (2076 cm^{-1}). This difference may reflect a greater degree of dipole–dipole coupling between CO molecules on the planar Pt(111) surface.[16]

Further studies of the carbonyl vibrational properties in cluster and surface electrochemical environments, including single crystals, are underway.

Acknowledgment. This work is supported by the National Science Foundation, via Grants CHE-86-16697 (to L.F.D.) and CHE-88-18345 (to M.J.W.). We are indebted to Johnson-Matthey Inc., Metal Loan Program (West Deptford, NJ), for supplying a sample of chloroplatinic acid, from which the platinum carbonyl clusters were prepared.

---

[9] For further experimental details of the FTIR spectroelectrochemical procedures, see: (a) Corrigan, D. S.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 5300. (b) Corrigan, D. S.; Leung, L.-W. H.; Weaver, M. J. *Anal. Chem.* **1987**, *59*, 2252. (c) Leung, L.-W. H.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 4019.

[10] (a) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054. (b) Cirjak, L. M.; Ginsburg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940. (c) Kubat-Martin, K. A.; Barr, M. E.; Spencer, B.; Dahl, L. P. *Organometallics* **1987**, *6*, 2570.

[11] Lewis, G. J.; Dahl, L. F., unpublished results.

[12] For example, see: (a) Lambert, D. K. *J. Chem. Phys.* **1988**, *89*, 3847 and references therein. (b) Mehandru, S. P.; Anderson, A. B. *J. Phys. Chem.* **1989**, *93*, 2044.

[13] Roth, J. D.; Weaver, M. J., unpublished results.

[14] The smaller potential ranges over which the odd-electron species ($n = -1, -3, -5$) are stable is consistent with the known tendency of Pt complexes to possess an even electron count with no unpaired electrons.

[15] Chang, S. C.; Leung, L.-W. H.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 5341.

[16] Olsen, C. W.; Masel, R. I. *Surf. Sci.* **1988**, *201*, 444.

Metal-Mediated Addition of Carbon Dioxide to the Activated Benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$

Joseph A. Corella II and N. John Cooper*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received September 25, 1989

The benzene ligand in $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) can be activated toward electrophiles by naphthalenide reduction to a dianionic species, formulated as the η^4-benzene complex $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ ($\mathbf{1}^{2-}$).[1] Electrophiles add to the arene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ under exceptionally mild conditions to give substituted cyclohexadienyl complexes,[1] and the established potential of such species as intermediates in the modification of simple arenes[2] has led us to explore the range of carbon-centered electrophiles that can add to $\mathbf{1}^{2-}$.

Although $PhCH_2Cl$ successfully adds to $\mathbf{1}^{2-}$, substrates such as CH_3I, $CH_3CH_2CH_2I$, and $(CH_3)_2CHBr$ oxidize $\mathbf{1}^{2-}$ to **1**. This is consistent with initial single-electron transfer (SET) to generate a halide anion and an organic radical, and it is only when SET leads to a relatively stable radical (such as benzyl) that recombination can allow carbon–carbon bond formation. This reasoning led us to search for acidic electrophiles with a tendency to react by two-electron pathways. Previous experience with the addition of CO_2 to dianionic transition-metal complexes[3] suggested that CO_2 would fit these reactivity requirements, and CO_2 does indeed add to the activated η^4-benzene in $\mathbf{1}^{2-}$ to give an intermediate cyclohexadienyl carboxylate complex, which can be oxidized and silylated to form $[Cr(\eta^6\text{-}C_6H_5CO_2SiMe_3)(CO)_3]$ (**5**). As shown in Scheme I, the unprecedented addition has a surprising endo stereochemistry, as established by ^{1}H NMR spectra of the silylated cyclohexadienyl complex $\mathbf{6}^{-}$.

Carbon dioxide (34.7 mL, 1.55 mmol) was added by syringe to a solution of $\mathbf{1}^{2-}$ that had been prepared as described previously[1] by potassium naphthalenide (0.24 M) reduction of **1** (0.302 g, 1.41 mmol) in tetrahydrofuran (THF, 30 mL) at −78 °C. This

---

[1] Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.

[2] (a) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36. (b) Jaouen, G. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 59. (c) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

[3] (a) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (c) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

0002-7863/90/1512-2832$02.50/0