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In Situ Infrared Spectroelectrochemistry Studies of Ferrocene, $[Rh_2(dimen)_2(dppm)_2](PF_6)_2$, and (mes)$Cr(CO)_3$ (dimen = 1,8-Diisocyanomenthane; dppm = Bis(diphenylphosphinomethane); mes = Mesitylene). A Useful Technique for the Characterization of Electrochemically Generated Organometallic Species

Sir:

During the years since spectroelectrochemistry has been in use,[1-5] many important applications to inorganic chemistry have been reported by several different groups. Many of these studies involved the use of transmission spectroscopy in the UV-visible spectral region.[1-6] One of the most commonly used cell designs for these studies is the optically transparent thin-layer electrochemical (OTTLE) cell with a gold minigrid electrode.[2-5,7,8] OTTLE studies have been used to obtain spectra of electrochemically generated products[3,6,9-11] and to measure the standard potentials of redox couples in the presence and absence of mediators.[12-14] This general area is well developed as judged by a recent review.[15]

Spectroelectrochemical studies that utilize the OTTLE cell design in the UV-visible spectral region have many advantages for product identification and for mechanistic studies of transition metal complexes in solution. Among these are small electrolysis volumes that yield short electrolysis times, rapid time response for the measurement of kinetic parameters, and the rapid, in situ generation of reactive species with stability properties that preclude isolation. With all these advantages, OTTLE studies in the UV-visible spectral region suffer a major drawback for the structural characterization of solution species because electronic absorption spectroscopy does not yield the readily interpretable structural information that can be obtained from infrared spectral measurements.

Although studies that utilize transmission infrared spectroelectrochemistry have been reported,[16-19] the technique is not fully developed. In this communication, we wish to report some of our preliminary studies of in situ transmission infrared spectroelectrochemistry that utilize an OTTLE with a gold minigrid working electrode. These studies not only demonstrate the utility of the technique for several organotransition metal systems of interest to us but also illustrate the technique as a general tool for inorganic and organometallic chemists.

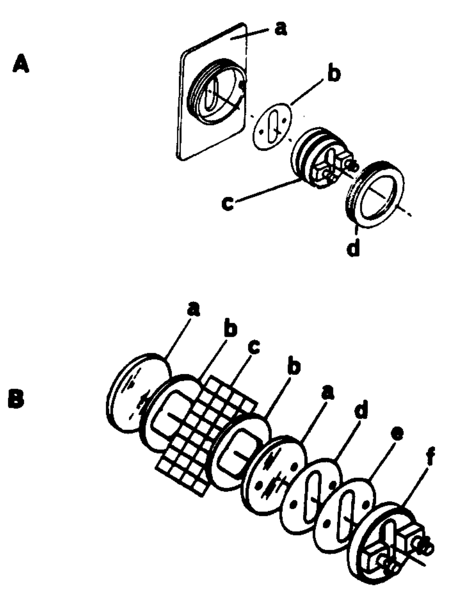

Figure 1. (A) Diagram of the infrared OTTLE and cell holder: (a) back plate; (b) Teflon gasket; (c) salt plate/minigrid electrode assembly (see Figure 1B); (d) knurled end cap. (B) Expanded view of the salt plate/minigrid assembly depicted as component c in Figure 1A: (a) NaCl salt plates; (b) Tefzel gaskets; (c) gold minigrid electrode; (d) indium gasket; (e) Teflon gasket; (f) needle plate.

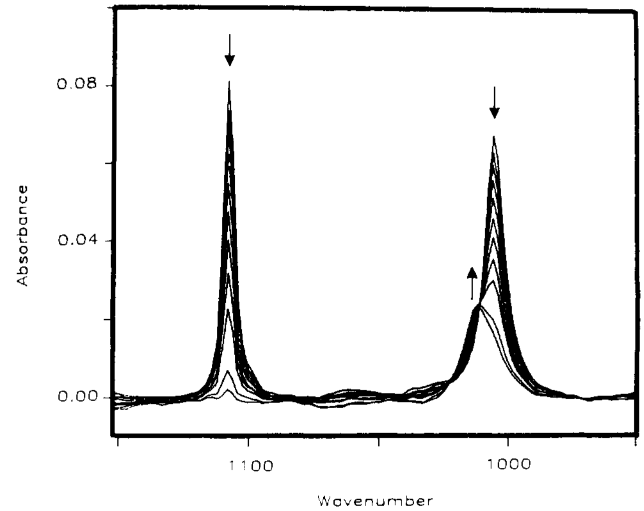

Figure 2. Infrared spectral changes that result during the electrolysis of a 0.018 M solution of ferrocene in CH_2Cl_2/TBAH at +1.25 V in the IR-OTTLE. The arrows indicate the direction of change. Peaks at 1107 and 1005 cm^{-1} decrease in intensity as the 1011-cm^{-1} band increases in intensity.

Our cell design[20] (Figure 1) is similar to one previously described[16] with some improvements. A piece of 100 lines/in. gold minigrid was hermetically sealed between drilled and undrilled 32-mm-diameter NaCl plates by melt-sealing the grid to the plates between two intervening Tefzel gaskets. The plates were compression sealed to a standard needle plate with thin indium or Teflon gaskets. This entire unit was held in a standard, commercially available IR cell holder. Connection between a copper wire and an exposed portion of the gold minigrid was made with silver epoxy. The auxilliary and reference electrodes were placed in a glass tube outlet port. The solution of interest was degassed by bubbling with purified argon and loaded into the cell from a gastight 25-mL syringe. Many fillings of the OTTLE could be

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(1) Kuwana, T.; Darlington, R. K.; Leedy, D. W. *Anal. Chem.* **1964**, *36*, 2023.
(2) Murray, R. W.; Heineman, W. R.; O'Dom, G. W. *Anal. Chem.* **1967**, *39*, 1666.
(3) Kuwana, T.; Heineman, W. R. *Acc. Chem. Res.* **1976**, *9*, 241.
(4) Heineman, W. R. *Anal. Chem.* **1978**, *50*, 390A.
(5) Rhodes, R. K.; Kadish, K. M. *Anal. Chem.* **1981**, *53*, 1539.
(6) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134.
(7) Petek, M.; Neal, T. E.; Murray, R. W. *Anal. Chem.* **1971**, *43*, 1069.
(8) DeAngelis, T. P.; Heineman, W. R. *J. Chem. Educ.* **1976**, *53*, 594.
(9) Cornillon, J.-L.; Anderson, J. E.; Swistak, C.; Kadish, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 7633.
(10) Blubaugh, E. A.; Yacynych, A. M.; Heineman, W. R. *Anal. Chem.* **1979**, *51*, 561.
(11) Boyd, D. C.; Matsch, P. A.; Mixa, M. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3331.
(12) Heineman, W. R.; Kuwana, T.; Hartzell, C. R. *Biochem. Biophys. Res. Commun.* **1973**, *50*, 892.
(13) Sailasuta, N.; Anson, F. C.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 455.
(14) Reid, L. S.; Taniguchi, V. T.; Gray, H. B.; Mauk, A. G. *J. Am. Chem. Soc.* **1982**, *104*, 7516.
(15) Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 305.
(16) Heineman, W. R.; Burnett, J. N.; Murray, R. W. *Anal. Chem.* **1968**, *40*, 1974.
(17) (a) DuBois, D. L.; Turner, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4989. (b) DuBois, D. L.; Turner, J. A. *Inorg. Chem.* **1984**, *23*, 2047.
(18) Pons, S.; Foley, J. *Anal. Chem.* **1985**, *57*, 945A.
(19) (a) Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chim. Acta*, in press. (b) Brisdon, B. J.; Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chem.*, in press.
(20) The cell used in this study was constructed from the following materials: Au minigrid, 100 lines/in. (Buckbee-Mears); NaCl plates, 32 mm × 3 mm (Wilmad Glass Co., Inc.); cell holder (Wilmad Glass Co., Inc.); Tefzel gasket, 1000 gauge (E. I. Du Pont de Nemours & Co.); Ag epoxy (ACME Chemical & Insulator Co.); Leuer ground glass joint inlet/outlet ports (Kontes). Cell pathlength = 0.22 mm.

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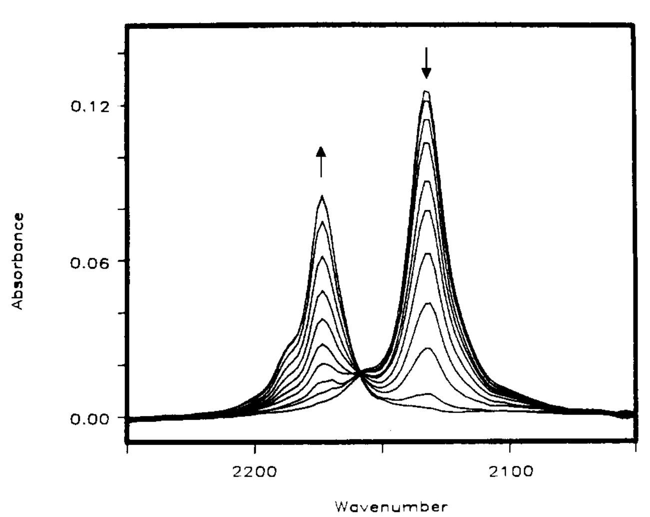

Figure 3. Infrared spectral changes that result during the electrolysis of a 9.9 × 10^{-4} M solution of $[Rh_2(dimen)_2(dppm)_2](PF_6)_2$ in CH_2Cl_2/TBAH at +1.5 V in the IR–OTTLE. The arrows indicate the direction of change. The peak at 2133 cm^{-1} decreases in intensity as the peak at 2173 cm^{-1} increases.

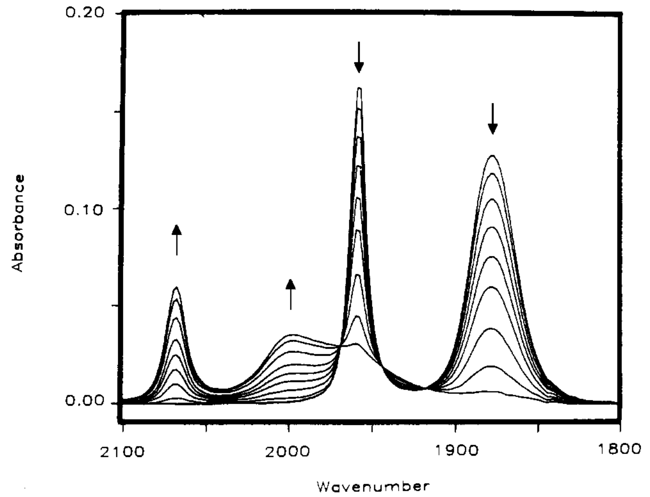

Figure 4. Infrared spectral changes that result during the electrolysis of a 2.1 × 10^{-3} M solution of $(mes)Cr(CO)_3$ at +1.15 V in the IR–OTTLE. The arrows indicate the direction of change. The peaks at 1959 and 1878 cm^{-1} decrease in intensity as peaks at 2067 and 1998 cm^{-1} and a shoulder at 1963 cm^{-1} increase in intensity.

made from one filling of the syringe. The cell was placed in the cell compartment of a Mattson Instruments Sirius 100 FT-IR spectrometer so that solutions could be pushed into the cell via polyethylene tubing. Background interferograms (eight scans) of pure solvent/electrolyte were taken and stored. The working solution was then pushed into the cell, and spectra were taken as the electrolysis proceeded. The interferograms were collected during the electrolysis, processed in the usual manner, and converted into absorbance spectra with the background subtracted.

One of our early experiments designed to evaluate the utility of the technique is illustrated in Figure 2. The spectra were taken at regular intervals during the electrolysis of an 18 mM solution of ferrocene in 0.1 M TBAH/CH_2Cl_2. The bands due to the antisymmetric ring breathing and the C–H bending (parallel) modes[21] of ferrocene at 1107 and 1005 cm^{-1}, respectively, decrease in intensity as a new band due to the C–H bending mode of the ferrocenium ion[22] grows in at 1011 cm^{-1}. In addition to yielding the effective volume of the cell and illustrating the expected quantitative interconversion of the ferrocene/ferrocenium redox forms, this experiment also demonstrates that even weak IR bands in any IR spectral region can be investigated provided the background absorbance of the solvent/electrolyte in the spectral region of interest is acceptably small.

A second application of the method is illustrated in Figure 3. We have recently shown[11] that metal-centered d^8–d^7 radical species are generated upon controlled potential electrolysis of binuclear d^8–d^8 Rh(I) complexes. We have previously studied the spectral properties of these reactive species by cyclic voltammetry, UV–visible OTTLE techniques, and EPR spectroscopy. Electrolysis of CH_2Cl_2/TBAH solutions of $[Rh_2(dimen)_2(dppm)_2]^{2+}$ (dimen = 1,8-diisocyanomenthane; dppm = bis(diphenylphosphinomethane)) in the IR–OTTLE cleanly generates the d^8–d^7 cation radical as evidenced by the maintainence of an isosbestic point in the ν(CN) stretching region of the IR spectrum. The increase in the ν(CN) stretching frequency upon oxidation is consistent with a decrease in the electron density of the d^8–d^7 radical relative to the d^8–d^8 parent species. In several electrolyses of this solution, the infrared spectra indicated that greater than 95% conversion had been achieved in about 4 min. Future improvements of the cell design should allow significant decreases in this total electrolysis time, but even the 4-min total electrolysis time allows one to monitor homogeneous chemical reactions that exhibit half-lives of about 1 min with very sensitive IR spectral identification. The results of such a study for the axial substitution reactions of $[Rh_2(dimen)_2(dppm)_2]^{3+}$ and the analogous $[Rh_2(TM4)_2(dppm)_2]^{3+}$ (TM4 = 2,6-dimethyl-2,6-diisocyanohexane) radicals will be reported at a future date.[23] The similarity of the UV–visible spectra of these axially substituted oxidation products precludes the conventional UV–visible OTTLE method as a viable tool to follow and identify the species involved in these reactions.

The last of the preliminary studies which we wish to report involves the generation of a reactive and previously uncharacterized organometallic intermediate. Several previous[24–35] workers have reported electrochemical oxidation of $(arene)Cr(CO)_3$ complexes. These complexes exhibit a one-electron oxidation to the Cr(I) radical cation with variable chemical reversibility. The reversibility depends on the nature of the arene ligand and the presence of nucleophiles in the solutions. For example, when the arene is mesitylene (mes), the complex[25] exhibits an oxidation at $E^{\circ\prime}$ = +0.58 V vs. SCE that is electrochemically and chemically reversible. Controlled-potential electrolyses of the mesitylene system have been reported[26] to generate the very moisture sensitive Cr(I) cation radical species $(mes)Cr(CO)_3^+$, but to date no spectral characterization of this radical has been reported. Oxidation of $(mes)Cr(CO)_3$ in the IR–OTTLE is shown in Figure 4 (total elapsed time 3.5 min). As previously reported, the electrolysis results in the production of a single species only under scrupulously dry conditions. The appearance of the two new ν(CO) stretching frequency bands at 2067 and 1998 cm^{-1}, and a shoulder at 1963 cm^{-1} in the oxidation product sugggest that the radical species has a geometry similar to that of the neutral complex. The splitting of the E mode into the 1998-cm^{-1} peak and 1963-cm^{-1} shoulder in the $(mes)Cr(CO)_3^+$ radical is probably due to slight lowering of the symmetry due to ion-pairing interactions.[36,37] This

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(21) Rosenblum, M. *Chemistry of the Iron Group Metallocenes*: Wiley-Interscience: New York, 1965; p 38.

(22) Fritz, H. *Adv. Organomet. Chem.* **1964**, 2, 278.

(23) Bullock, J. P.; Boyd, D. C.; Mann, K. R., work in progress.

(24) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

(25) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1769.

(26) Rieke, R. D.; Milligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* **1981**, *218*, C25.

(27) Degrand, C.; Radecki-Sudre, A.; Besancon, J. *Organometallics* **1982**, *1*, 1311.

(28) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

(29) Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* **1983**, *22*, 987.

(30) Peterleitner, M. G.; Tolstaya, M. V.; Krivykh, V. V.; Denisovitch, L. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1983**, *254*, 313.

(31) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 715.

(32) Ikeshoji, T.; Parker, V. D. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1112.

(33) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 175.

(34) Doxsee, K. M.; Grubbs, R. R.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819.

(35) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553.

result is consistent with the most recent study of (arene)Cr(CO)$_3$ electrochemistry[35] that suggests the radical species interacts with the supporting anion in CH_2Cl_2 solutions, and another study[34] that makes a similar observation for the less sterically hindered (C_6Me_6)W(CO)$_3$ system. The 100-cm^{-1} shift to higher energy for the A and E symmetry ν(CO) spectral bands of the oxidized (mes)Cr(CO)$_3^+$ was expected; however, the overall decrease in the integrated intensity exhibited by these bands is of additional interest and is perhaps indicative of a decrease in the transition dipole for these transitions in the (mes)Cr(CO)$_3^+$ complex.

In summary, we have demonstrated that the application of the IR-OTTLE technique can significantly aid in the structural characterization of electrochemically generated species that may be difficult to isolate. Homogeneous reactions of the electrogenerated species may also be conveniently studied by the technique. Future work we plan includes the improvement of the cell design to further decrease the electrolysis times and to obtain more accurate control of the working electrode potential.

Acknowledgment. We thank Professors John Evans, Harold Swofford, Lawrence Potts, and Peter Carr for several stimulating discussions, Johnson Matthey, Inc., for a generous loan of rhodium trichloride, and the NSF (Grant No. CHE 8509325) for the funds used to purchase the FT-IR spectrometer.

Registry No. [Rh_2(dimen)$_2$(dppm)$_2$](PF$_6$)$_2$, 103731-85-7; [Rh_2(dimen)$_2$(dppm)$_2$]$^{3+}$, 103731-86-8; (mes)Cr(CO)$_3$, 12129-67-8; (mes)Cr(CO)$_3^+$, 52826-61-6; Au, 7440-57-5; ferrocene, 102-54-5; ferrocenium, 12125-80-3.

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(36) The IR spectra of (arene)Cr(CO)$_3$ complexes have been studied previously: Davis, R.; Kane-Macquire, L. A. P. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, England, 1982; Vol. 4, p 1022.

(37) Davidson, G.; Riley, E. M. *Spectrochim. Acta, Part A* **1971**, *27A*, 1649.

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A Multiply Bonded Dimetal Complex of the M_2L_{10} Type That Contains π-Acceptor Ligands and Does Not Possess an Edge-Shared Bioctahedral Structure. The [Re_2Cl_3(μ-dppm)$_2$(CO)(CN-*t*-Bu)$_2$]$^+$ Cation

Sir:

The reactivity of the triply bonded dirhenium(II) complex Re_2Cl_4(μ-dppm)$_2$ (**1**) toward carbon monoxide, isocyanides, and nitriles is currently under investigation.[1] The facile M-M bond-cleavage reactions that can occur upon reacting multiply bonded dimetal species with CO and RNC ligands[2] can be prevented through the use of μ-$R_2PCH_2PR_2$ ligands. A structural feature common to the resultant complexes is that those which contain carbonyl ligand(s) seem to prefer edge-sharing bioctahedral structures, within which there is a [Re_2(μ-Cl)(μ-CO)(μ-dppm)$_2$] unit. Thus, **1** can be converted by CO into the A-frame-like complex Re_2(μ-Cl)(μ-dppm)$_2$Cl$_3$(CO),[3,4] which in turn reacts with 1 equiv of xylNC (xyl = 2,6-$Me_2C_6H_3$) and with xylNC (2 equiv)/TlPF$_6$ mixtures to give Re_2(μ-Cl)(μ-CO)(μ-dppm)$_2$Cl$_3$(CNxyl) (**2a**)[4] and [Re_2(μ-Cl)(μ-CO)(μ-dppm)$_2$Cl$_2$(CNxyl)$_2$]PF$_6$ (two isomers); (**3a**),[5] respectively.

We have reported previously the synthesis of the *t*-BuNC analogue of **2a**, viz., a complex of stoichiometry Re_2Cl_4(dppm)$_2$(CO)(CN-*t*-Bu) (**2b**), and noted that unlike **2a** it does not contain a bridging CO ligand (IR-active ν(CO)$_t$ mode at 1968 cm^{-1}).[4] Further reaction of **2b** with *t*-BuNC in acetone in the presence of TlPF$_6$ gives the complex [Re_2Cl_3(dppm)$_2$(CO)(CN-*t*-Bu)$_2$]PF$_6$ (**3b**), in which a terminal Re-CO bond is retained (ν(CO) at 1960 cm^{-1} for a Nujol mull).[5] The possibility that **3b** and, by implication, **2b** are of a structural type different from that encountered previously (i.e. different from an edge-shared bioctahedral geometry) has been examined. Herein we report the preliminary results of this investigation.

A batch of red-brown crystals of **3b** were grown from a CH_2Cl_2-CH_3OH solvent mixture, and a suitable single crystal was selected and subjected to an X-ray structure analysis. Subsequent analysis of the data indicated that the crystal was that of the salt [Re_2Cl_3(dppm)$_2$(CO)(CN-*t*-Bu)$_2$](PF$_6$)$_{0.5}$(OMe)$_{0.5}$.[6-10] The structure of the cation (Figure 1) is closely akin to that of a molecule of the M_2L_8 type,[11] with two additional ligands (chlorides) in axial positions. The *t*-BuNC ligands are trans to one another and their stereochemical disposition thereby resembles that of the nitrile ligands in the complexes [(RCN)$_2$ClRe(μ-dppm)$_2$ReCl$_2$]PF$_6$.[12] The Re-Re distance of 2.379 (1) Å is longer than that in [(PhCN)$_2$ClRe(μ-dppm)$_2$ReCl$_2$]PF$_6$ (2.270 (1) Å) but much shorter than the comparable distances (2.58-2.61 Å) found for formally dirhenium(II) complexes that are edge-sharing bioctahedra with [Re_2(μ-Cl)(μ-CO)(μ-dppm)$_2$] units, i.e. Re_2-

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(1) Price, A. C.; Walton, R. A. *Polyhedron* **1987**, *6*, 729 and references cited therein.

(2) (a) Dunbar, K. R.; Walton, R. A. *Inorg. Chim. Acta* **1984**, *87*, 185. (b) Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540.

(3) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524.

(4) Cotton, F. A.; Dunbar, K. R.; Price, A. C.; Schwotzer, W.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4843.

(5) Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A. H.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2717.

(6) Crystals of [Re_2Cl_3(dppm)$_2$(CO)(CN-*t*-Bu)$_2$](PF$_6$)$_{0.5}$(OCH$_3$)$_{0.5}$ are triclinic, space group $P\bar{1}$, with a = 12.125 (2) Å, b = 23.877 (4) Å, c = 11.694 (2) Å, α = 100.74 (1)°, β = 90.38 (1)°, γ = 76.34 (1) °, V = 3230 (2) Å^3, Z = 2, d_{calcd} = 1.574 g/cm^3, and μ = 40.90 cm^{-1}. X-ray diffraction data were collected at 22 °C on a 0.17 × 0.14 × 0.05 mm crystal for 8394 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD4 diffractometer using graphite-crystal-monochromated Mo Kα radiation (λ = 0.71073 Å). Details of the crystal data collection and reduction methods are the same as those described elsewhere.[7] An empirical absorption correction was applied,[8] but no correction for extinction was made. During the course of the structure analysis it became apparent that there was only one PF_6^- anion for the two dirhenium cations in the unit cell. This did not satisfy the charge requirements for this complex. The largest peak in the difference Fourier map at this stage was less than 2.5 e/Å^3. Subsequent refinement of this residual electron density suggested the presence of a small molecule, which we concluded could be a methoxide anion. This lies on a general position and is disordered within the unit cell. Refinement was carried out on this assumption.[9] Accordingly, there is a total of two anions per unit cell, each occupying sites of half-occupancy. All atoms except the C and O atoms of the methoxide anion were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[10] Hydrogen atoms were not included in the least-squares refinement. The final residuals were R = 0.038 and R_w = 0.063 for 6512 data with $I > 3\sigma(I)$. The IR spectrum (Nujol mull) and cyclic voltammogram of the crystals were found to be the same as those of the bulk synthetic batches of the complex **3b**. This sample was also, as expected, ESR-silent (1:1 CH_2Cl_2/toluene at -150 °C) in accord with the expected diamagnetism of the cation. The ^{1}H NMR spectrum of these crystals (recorded in (CD$_3$)$_2$CO) showed a resonance at δ +3.33 that we attribute to methanol (CH_3); this could form through the reaction of methoxide anion with trace amounts of water present in the solvent.

(7) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

(8) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(9) The identification of methoxide ion in the structures of transition-metal complexes is not without precedent. See, for example: Bino, A. *J. Am. Chem. Soc.* **1987**, *109*, 275.

(10) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Weber, J. T. *Ibid.*, Table 2.2B.

(11) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

(12) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 1258.

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