the lowest excited state of $Re_2Cl_8^{2-}$ is unreactive.[4] Finally, the related metal carbonyl, $(\eta\text{-}C_5H_5)_2V_2(CO)_5$, having a V═V double bond appears to lose CO as the primary photoreaction; it is not known whether this is an upper excited-state process.[12]

Conclusions

We conclude that the excited states produced by >254-nm irradiation of $(\eta\text{-}C_5R_5)_2Cr_2(CO)_4$ do not reduce the Cr≡Cr bond order sufficiently to allow dissociative Cr≡Cr cleavage to compete with Cr—CO cleavage. Thus, we have been unable to photogenerate 15-e fragments from the M≡M triple bonded species. Reactive $(\eta\text{-}C_5R_5)_2Cr_2(CO)_3$ fragments are produced with a quantum efficiency that is highest in the ultraviolet and does not exceed 10^{-1}. It is not known whether the excitation energies used actually exceed the Cr≡Cr bond dissociation energy. Therefore, we cannot uneuivocally conclude that fast alternative decay channels (e.g., CO loss) prevent the Cr≡Cr scission.

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Fluxionality and Basicity of $Cp_2Re_2(CO)_5$

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$(C_5H_4R)_2Re_2(CO)_5$ (R = H and Me) both exhibit rapid interchange of their three distinct CO environments at −83 °C. This proceeds by a nondissociative mechanism. Enantiomerization of the molecule is also demonstrated to occur in the same temperature range with use of ^1H and ^{13}C NMR. A transition state devoid of bridging carbonyls is proposed for this process. Both dimers are protonated ($HOSO_2CF_3$ at low temperatures) at the Re–Re bond to give a stereochemically rigid product. The ν(CO) value of the bridging carbonyls in the protonated and deprotonated forms are essentially identical; an explanation of this unusual result is proposed.

Introduction

The question of the site of protonation of dimeric and cluster metal carbonyl derivatives is a matter of longstanding interest. Protonations at a metal–metal bond[1,2] and at a carbonyl oxygen[3] are viable alternatives. The work of Shriver,[4–6] which has also employed aluminum acids and carbonium ion precursors, has shown that bridging carbonyls are more basic then terminal carbonyls. More recently, the work of Fachinetti,[7] Keister,[8] and Shriver[9] employing low-valent metal clusters containing μ- and μ_3-CO ligands has shown that protonation (or alkylation) at carbonyl oxygen will sometimes induce an intramolecular electron transfer in which metal electrons serve to reduce CO to methanol or methane. Such transformations may mimic the Fischer–Tropsch activation of CO at a multimetallic site on a catalytic surface.

We report here our observations concerning both the fluxionality and basicity of $Cp_2Re_2(CO)_5$,[10] which contains the longest[11] metal–metal bond yet observed to be bridged by CO.[12]

Experimental Section

General Data. Reactions and spectroscopic studies were carried out under nitrogen with use of solvents dried by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in the Fourier transform mode on a Varian XL 100-15 spectrometer. Some ^1H NMR spectra were also recorded on a Varian HR-220 spectrometer. $C_5H_5Re(CO)_3$ was prepared by two methods,[13,14] with the latter giving higher yield and purer product. $^{13}C\{^1H\}$ NMR (in $CDCl_3$ at 35 °C): δ 193.4 (CO), 84.3 (C_5H_5). ^1H NMR: δ 5.35 (in $CDCl_3$), 4.40 (in C_6D_6). $ReCl(CO)_5$ required in the latter synthesis was produced as reported.[15]

$(C_5H_4CH_3)Re(CO)_3$. This was prepared by the reaction of $NaC_5H_4CH_3{\cdot}MeOCH_2CH_2OMe$[16] (3.3 g, 17 mmol) with equimolar $ReCl(CO)_5$ in benzene. Following overnight reflux, the solvent was removed under vacuum. Sublimation (70 °C, 0.1 mmHg) of the solid residue yielded colorless crystals of the product in 80% yield. IR (in hexane): 2030 (s), 1935 (vs) cm^{-1}. ^1H NMR (in C_6D_6): δ 4.33 (s, ring protons), 1.57 (s, CH_3). Mass spectrum (EI): $(C_5H_4CH_3)Re(CO)_n^+$, n = 0–3. $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 194.2 (CO), 106.5 (ipso C), 83.7 and 83.0 (unsubstituted ring carbons).

$(C_5H_5)_2Re_2(CO_5$ (Ia) was synthesized according to the literature.[10] Irradiation (254 nm, Rayonet reactor) in a quartz reactor tends to deposit the hexane-insoluble product on the outer reactor walls; this problem is minimized by employing a water-cooled glass spiral insert in the reactor, which has the effect of encouraging crystallization of the product on the cooled spiral. The IR and ^1H NMR (δ 4.67 in C_6D_6) agree with those reported.[10] The EI mass spectrum shows the ions $Cp_2Re_2(CO)_n^+$, n = 0–5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2 with 0.05 M $Cr(acac)_3$): δ 207.48 (5 CO), 88.6 (C_5H_5) (at +25 and −83 °C). This compound and **Ib** are only mildly air sensitive in solution.

$(C_5H_4CH_3)_2Re_2(CO)_5$ (Ib) was synthesized analogously, by photolysis of $(C_5H_4Me)Re(CO)_3$ in hexanes. The solution IR (carbonyl region) is identical with that of Ia. ^1H NMR (220 MHz in CD_2Cl_2 at 16 °C): δ 5.22 and 5.14 (AA′BB′ pattern of two "triplets" (2 Hz splitting) due to ring protons), 2.08 (s, CH_3). $^{13}C\{^1H\}$ NMR (at −70 °C in CD_2Cl_2): δ 209.3 (5 CO), 108.3 (2, substituted ring carbons), 88.0 and 85.9 (4 each, ring carbons), 12.7 (2, CH_3).

Test of Dimer Scission. $(C_5H_4CH_3)Re(CO)_3$ (0.015 g, 0.044 mmol) and $(C_5H_5)_2Re_2(CO)_5$ (0.024 g, 0.037 mmol) were combined in 1 mL C_6D_6. After 50 h, the ^1H NMR was invariant (integration vs. an internal standard); no new peaks were observed.

Attempted Exchange of ^{13}CO with $Cp_2Re_2(CO)_5$. A THF solution of $Cp_2Re_2(CO)_5$ is stable (i.e., no $CpRe(CO)_3$ is produced) under 1

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atm of CO in 10 h. In a separate experiment, no exchange was evident (IR analysis) upon vigorous stirring of $Cp_2Re_2(CO)_5$ (0.01 g, 0.02 mmol) and ^{13}CO (0.28 mmol) in 5 mL of THF at 25 °C for 8 h.

Protonation of $(C_5H_5)_2Re_2(CO)_5$. (a) $Cp_2Re_2(CO)_5$ (0.06 g, 0.09 mmol) was dissolved in CH_2Cl_2 under nitrogen in an NMR tube and cooled to −78 °C. $HOSO_2CF_3$ (8 μL, 0.09 mmol) was slowly added to this cold solution with a syringe. The NMR tube was shaken and quickly transferred to the probe of a 220-MHz ^1H NMR spectrometer which was held at +16 °C. A resonance was observed at δ −9.9; this persisted for over 30 min in the NMR probe.

(b) The addition of $HOSO_2CF_3$ (0.15 mL, 1.7 mmol) to an NMR tube containing $Cp_2Re_2(CO)_5$ (0.06 g, 0.09 mmol) in 0.5 mL of CD_2Cl_2 at −70 °C produced new resonances at δ 5.94 and −9.80 (100 MHz). Consumption of $Cp_2Re_2(CO)_5$ is complete, and separate resonances are seen for the hydride and free $HOSO_2CF_3$; intermolecular exchange is slow. Warming this solution to +10 °C causes growth of the resonance due to $CpRe(CO)_3$.

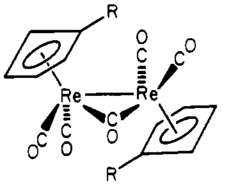
(c) The addition of $HOSO_2CF_3$ (27 μL, 0.3 mmol) to $(C_5H_5)_2Re_2(CO)_5$ (0.2 g, 0.3 mmol) in 3 mL of CD_2Cl_2 was carried out at −43 °C. The $^{13}C\{^1H\}$ NMR, at −43 °C, shows, in addition to the ring carbon signal of $CpRe(CO)_3$, a singlet at δ 90.5. $Cp_2Re_2(CO)_5$ had been completely consumed. Low solubility and an unfavorable relaxation rate ($Cr(acac)_3$ reacts with $HOSO_2CF_3$) prevent detection of the carbonyl resonances.

(d) An attempt was made to trap the emerging "$CpRe(CO)_2H^+$" fragment postulated to be formed when a solution of $Cp_2Re_2(CO)_5H^+$ is warmed. To the solution in part C was added (at −20 °C) tetrapropylammonium iodide (0.1 g, 0.32 mmol) in 1 mL of CD_2Cl_2. This causes the appearance of a new ^{13}C resonance at δ 90.7. After the solution was warmed to 25 °C, the ^1H NMR shows the cyclopentadienyl resonance of $CpRe(CO)_3$ and a second peak at δ 5.82. The infrared spectrum of this same CD_2Cl_2 solution shows bands at 2050 and 1980 cm^{-1}, in addition to those of $CpRe(CO)_3$.

Protonation of $(C_5H_4CH_3)_2Re_2(CO)_5$. Compound Ib (0.04 g, 0.06 mmol) and $HOSO_2CF_3$ (0.2 mL, 2 mmol) were combined at −70 °C in CD_2Cl_2. The $^{13}C\{^1H\}$ NMR of this solution (at −70 °C) showed carbonyl resonances at δ 196.3 and 191.7. *All* ring carbons in this product, $(C_5H_4CH_3)_2Re_2(CO)_5H^+$, are inequivalent, appearing at δ 112.7, 91.4, 89.9, 89.3, and 86.8; a single CH_3 resonance appears at δ 12.4. All resonances of $(C_5H_4CH_3)Re(CO)_3$ were evident in small amounts; Ib was completely consumed in this experiment.

Results

Fluxionality. Dimeric $(C_5H_5)_2Re_2(CO)_5$ (Ia) undergoes a



Ia, R = H
b, R = CH_3

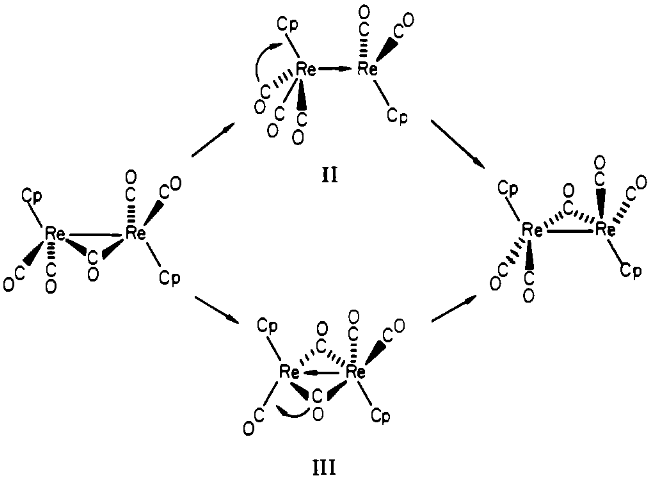
dynamic process which interchanges all five carbonyls (three distinct environments). This process is rapid on the ^{13}C NMR time scale both at 25 and −83 °C. Throughout this temperature range, the only changes detected are a slight (~0.5 ppm) temperature dependence of the chemical shift and, at the lowest temperature, some viscosity broadening. Infrared data affirms that the bridging carbonyl is retained in solution, and the single carbonyl resonance is sufficiently far downfield (207 ppm; cf. $CpRe(CO)_3$ at δ 193.4) to be consistent with a 1:4 average of bridge and terminal chemical shifts. The bridging carbonyl ^{13}C NMR resonance in the related compound $Cp_2Mn_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C_3H_4)$ appears at 275 ppm.[17]

It is possible to show that dimer scission (eq 1) is not the

$$Cp_2Re_2(CO)_5 \rightleftharpoons CpRe(CO)_3 + CpRe(CO)_2 \qquad (1)$$

mechanism of this carbonyl scrambling. Thus, combining dimeric $(C_5H_5)_2Re_2(CO)_5$ with monomeric $(C_5H_4CH_3)Re(CO)_3$ in C_6D_6 at 25 °C produced neither the mixed dimer $(C_5H_5)(C_5H_4CH_3)Re_2(CO)_5$ nor $(C_5H_5)Re(CO)_3$, both of which would be the consequence of eq 1; it was confirmed that the ^1H NMR resonances of both products would have been detectable if they had formed.

Scheme I



Dissociation of carbon monoxide is also not responsible for the CO scrambling. Thus, under conditions where this scrambling is rapid, ^{13}CO if not incorporated into $Cp_2Re_2(CO)_5$. It follows that the CO site exchange is a nondissociative (intramolecular) process.

Complexes Ia and Ib are chiral. The ortho (and meta) ring protons in Ib are therefore diastereotopic in the static structure; barring accidental equivalence, four ring proton chemical shifts and five ring carbon shifts are predicted. It follows from the observed two ring proton shifts and three ring carbon shifts that the two enantiomers are interconverted rapidly at 25 °C (we view accidental degeneracy in *both* ^{13}C and ^1H NMR as excessively coincidental). Although not rigorously required by the available spectral observations, we propose that enantiomerization and CO scrambling are effected by a single physical process. This will be true if the rearrangement which scrambles the carbonyl in Ib also generates a time-averaged mirror plane containing the two ring centers of gravity and the two metal atoms. Structures II and III (Scheme I) each represent transition states for CO migration which embody this feature. Repetitive application of either rearrangment process shown in this scheme accomplishes both the enantiomerization and the equivalencing of all CO environments.

Basicity. The bridging carbonyl stretching frequency in complexes Ia and Ib is sufficiently low (1740 cm^{-1}) that the associated oxygen becomes a potential site of protonation. We have demonstrated protonation of the $=CH_2$ group in the valence-isoelectronic species $Cp_2Mn_2(CO)_4(\mu\text{-}CCH_2)$.[17] The nitrogen atom of the bridging nitrile in $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNR)$ has been both protonated[18] and alkylated.[19]

Trifluoroacetic acid (2.5 equiv) does not effect protonation of Ia in CD_3CN. Protonation of complex Ia with equimolar $HOSO_2CF_3$ at −78 °C gives essentially complete conversion to an unstable dark red complex which exhibits a resonance at δ −9.9 (in CH_2Cl_2), characteristic of protonation at the metal.[20] The observation that all ten ring carbons (and all ten hydrogens) are equivalent is consistent with a μ-hydrido

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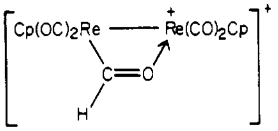
structure for $Cp_2Re_2(CO)_5H^+$. The available data are accommodated if the basic heavy-atom structure (i.e., the C_2 axis) of I is retained upon protonation at the Re–Re bond. The infrared spectrum of $Cp_2Re_2(CO)_5H^+$ at −78 °C (low-temperature IR cell) confirms that the bridging carbonyl is retained upon protonation; carbonyl stretches are observed at 1991, 1951, and 1720 cm^{-1} in CH_2Cl_2. Specifically excluded is conversion of a carbonyl group to a μ-formyl, as in IV.



IV

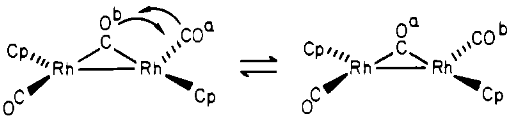
The carbon atoms of the $C_5H_4CH_3$ ring in Ib serve as a useful probe of dynamic stereochemistry subsequent to protonation. $(C_5H_4CH_3)_2Re_2(CO)_5H^+$, formed by protonation of Ib with $HOSO_2CF_3$ at low temperature, exhibits only one methyl ^{13}C NMR resonance, consistent with a structure of C_2 symmetry (protonation at the Re–Re bond and opposite to the μ-CO). Two equally intense ^{13}C NMR signals are observed in the terminal carbonyl region. No signal assignable to the single bridging carbonyl was detectable, due possibility to selective broadening by quadrupolar rhenium. In accord with the stereochemical rigidity deduced from the carbonyl region ^{13}C NMR, the diastereotopic ring carbons ortho to the methyl substituent are inequivalent in $(C_5H_4CH_3)_2Re_2(CO)_5H^+$. The meta carbons (also diastereotopic) are similarly inequivalent. It follows that neither carbonyl scrambling nor enantiomerization occur at −70 °C in $(C_5H_4CH_3)_2Re_2(CO)_5H^+$; protonation significantly impedes the intramolecular rearrangment which is so facile in Ia and Ib.

$[(C_5H_4R)_2Re_2(CO)_5H]SO_2CF_3$ is not stable in solution above about −40 °C. The readily identifiable product of its decomposition is the very stable monomer $(C_5H_4R)Re(CO)_3$. The remaining fragment, possibly "$(C_5H_4R)Re(CO)_2H^{+}$" coordinated by solvent or $SO_3CF_3^-$, is not readily stabilized and detected. We have attempted to capture this ion by warming the cationic monohydride dimer in the presence of $[NPr_4]I$. Under these conditions, with equimolar iodide added, we can observe inefficient capture of this dicarbonyl hydride fragment. The product of such scavenging has infrared and ^1H NMR spectra consistent with one of the isomers of $CpRe(CO)_2HI$ reported previously.[22]

Discussion

$Cp_2Re_2(CO)_5$ is a highly fluxional species, particularly in view of its long metal–metal bond (2.957 Å). Although there is no evidence for an *isomer* of structure II in solution, we suggest that the low activation energy for CO scrambling and enantiomerization may be a consequence of the instability of the "stretched" μ-CO unit in I. This would lower the activation energy required to reach transition state II.

In pursuing the metal cluster/metal surface analogy as it pertains to addend migration, Muetterties has noted[23] that the observed scrambling of all three CO ligands in $Cp_2Rh_2(CO)_3$ *may* occur by a mechanism which is geometrically suitable ("suprafacial") for flat metal surfaces (eq 2). Alternatively, it may occur by a mechanism ("antrarafacial") which is precluded for surfaces (eq 3), since it involves the μ-CO sequentially occupying positions on both sides of the Rh–Rh bond. This currently unanswered mechanistic point concerning $Cp_2Rh_2(CO)_3$ in fact amounts to asking whether or not the CO scrambling mechanism also effects enantiomerization of the dimer. For Ib, the simplest explanation of the two concurrent (in temperature) rearrangments is that these are effected by a single mechanism. The molecule thus utilizes the full set of spatial degrees of freedom available to it.



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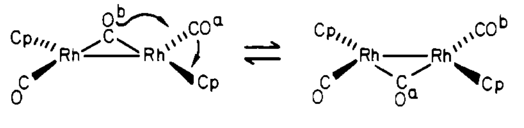

(3)

Infrared and ^1H NMR spectral data indicate that the unique proton in $(C_5H_4R)_2Re_2(CO)_5H^+$ is located at the metal–metal bond and not at the oxygen of the μ-CO. Because this compound is thermally unstable, we cannot be certain whether this is the kinetic or the thermodynamic product. Protonation of $Cp_2Rh_2(CO)_3$ likewise occurs at the Rh–Rh bond and not the bridging carbonyl. Here the bridging hydride chemical shift is δ −10.7.[24] This preference for metal protonation may be a consequence of the general increase in metal basicity (electron density) as one moves down any group of the periodic table.[25] It is also noteworthy that all previous examples of O protonation have involved *anionic* carbonyl complexes. Moreover, Keister's study of the protonation of $HRu_3(\mu\text{-}CO)(CO)_{10}^-$ shows that O-protonation is only kinetically, not thermodynamically, favored.[21] Protonation of Ia and Ib at the metal–metal bond and not at a single metal atom (to form an asymmetric dimer) is consistent with the fact that neither of the species $(C_5H_4R)Re(CO)_3$ (R = H or Me) is protonated by $HOSO_2CF_3$ under the conditions employed for I. The metal–metal bond is thus a basic (i.e., oxidizable) site which confers on dimers and clusters a reactivity which is absent in closely related monomers.

Protonation of I causes an increase in the activation energy of CO scrambling. This is a somewhat unusual result in view of the high mobility typically associated with hydride ligands and may be associated with ion pairing to the $O_3SCF_3^-$ anion in our salt. Ion pairing inhibits the fluxionality of $HFe_3(CO)_{11}^-$ salts.[26]

It is significant that protonation of the Re–Re bond in $Cp_2Re_2(CO)_5$ leaves the bridging carbonyl stretching frequency *unchanged* (Ia has a band at 1720 cm^{-1} in CH_2Cl_2), while the terminal frequencies undergo the expected shift to higher energy upon protonation (the strongest terminal stretches of Ia in CH_2Cl_2 appear at 1950 and 1911 cm^{-1}). Herrmann[24] has reported this same invariance of the μ-CO infrared frequency to protonation of the Rh–Rh bond in $Cp_2Rh_2(CO)_3$. The invariance of the bridging carbonyl frequency may indicate that back-bonding is *not* a significant feature of that structural unit (at least in complex I and in $Cp_2Rh_2(CO)_3$); instead, the low CO frequency which characterizes μ-CO units may be due mainly to a degree of rehybridization at carbon (from sp) dictated by the M–C–M angle.

Alternatively, the invariance of the bridging carbonyl frequency for these protonated dimers may be due to two competing factors. Protonation of a metal–metal bond is known to lengthen that bond.[27] This requires rehybridization of the bridging carbonyl carbon increasingly toward sp^2 and a con-

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sequent decrease in ν(CO). Since this counteracts the predicted rise in ν(CO) based solely on a back-bonding criterion, net cancellation is possible.

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Registry No. Ia, 36250-00-7; Ib, 76391-66-7; $Cp_2Re_2(CO)_5H^+$, 76391-67-8; $(C_5H_4CH_3)_2Re_2(CO)_5H^+$, 76391-68-9; $(C_5H_4CH_3)Re(CO)_3$, 33309-95-4; $ReCl(CO)_5$, 14099-01-5; $HOSO_2CF_3$, 1493-13-6.

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Preparation and Structure of Ethylenediaminetetraacetate Complexes of Ruthenium(II) with Dinitrogen, Carbon Monoxide, and Other π-Acceptor Ligands

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Complexes of $Ru^{II}(H_n edta)L_n$ (n = 1, 2; L = N_2, CO, NO, RCN) were prepared by reacting aqueous solutions of $Ru^{II}(Hedta)H_2O^-$, formed by reducing $Ru^{III}(Hedta)H_2O$ with H_2 on platinum black, with the appropriate ligand. In the case of L = N_2, a terminal complex and a bridging complex were identified in solution and were isolated as solid derivatives by using alternative procedures. $(Ru(edta))_2N_2^{4-}$ was found to dissociate at 25 °C with $\Delta H^* = 44$ kJ mol^{-1} and $\Delta S^* = -140$ J K^{-1}. The complexes were characterized by analytical and spectroscopic procedures, including ^{13}C NMR, and were shown to accommodate L, in both the tetradentate and pentadentate complexes, in the equatorial positions. The electronic and vibrational spectra of the complexes were found to be analogous with those of the corresponding ruthenium(II) tetraammine and pentaammine complexes with the same L.

Introduction

Ruthenium(II) and osmium(II) are the only metal centers which are known to form mononuclear and binuclear dinitrogen complexes in which the other ligands are σ donors with no π-acceptor capabilities. Thus, pentaammine,[1] tetraammineaquo,[2] bis(ethylenediamine)aquo,[3] triethylenediaminebromo and -aquo,[4] and pentaaquo[5] complexes of ruthenium(II) have been reported in which the sixth coordination position is occupied by terminal or bridging dinitrogen, often by direct substitution of an aquo ligand. The sixth coordination site in these complexes can also attach other π-accepting ligands such as CO,[6] HCN,[7] N_2O,[8] RCN,[9] and NO^+.[10]

Ethylenediaminetetraacetate, although normally a hexadentate ligand, can form six-coordinate complexes in which only five[11,12] or even four[13,14] of the potential donor atoms in the ligand are attached to the metal, the remaining coordination positions being occupied by other ligands. Ruthenium(III) also forms chloro complexes of this type,[15] which, in dilute acid solution, give rise to the uncharged species $Ru(Hedta)H_2O$.[16] It was considered that the ruthenium(II) complex formed by the reduction of the above species would contain a coordination site which, by analogy with the ammine complexes, would bind dinitrogen and other π-acceptor ligands. This paper reports the preparation and chemistry of such complexes of ruthenium(II) with ethylenediaminetetraacetate. Recently the reaction of $Ru^{III}(edta)H_2O^-$ and $Ru^{II}(edta)H_2O^{2-}$ with a number of ligands to form pentadentate complexes has been reported.[17] Acetonitrile and a number of nitrogen heterocyclic bases were shown to substitute in the ruthenium(II) system; however, no solid derivatives were reported as isolated or characterized.

Experimental Section

Materials. Hydrated ruthenium trichloride, $RuCl_3 \cdot nH_2O$, was purchased from Johnson and Matthey; analytical grade chemicals were used in all cases. Gases were obtained from CIG Australia Ltd. High-purity nitrogen and industrial hydrogen, argon, and carbon monoxide were used as received. Dinitrogen oxide was passed through chromous chloride to remove oxygen and then through P_2O_5 towers. Nitric oxide was purged by passing through concentrated sulfuric acid, through a cold trap, and finally over potassium hydroxide pellets.

Analyses. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and by the Levels Institute of Technology, Adelaide. The ruthenium(II) content of reduced $Ru^{III}(edta)H_2O^-$ solutions was estimated by reducing a solution of Fe(III) and determining the Fe(II) formed as the phenanthroline complex spectrophotometricaly.[18a] Magnesium was estimated by edta titration.[18b]

Physical Measurements. Solid-state infrared spectra were obtained from KBr pellets and Nujol mulls with use of a Perkin-Elmer spectrometer, Model 457; Raman spectra were recorded at the University of Tasmania with use of a Rhodamine 6G dye laser at 587.7 nm. Electronic spectra were recorded under dinitrogen with use of a

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