the chemical reduction of $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$ using magnesium metal (alternatively, sodium can be used), we produced a red oil which proved difficult to characterize. However, the corresponding magnesium reduction of $[Mo(CNPh)_5(dppe)](PF_6)_2$ produced an air-sensitive red solid whose CV displayed oxidations at $E_{p,a}$ = +0.42 V and $E_{1/2}$ = −0.27 V vs. SCE as well as a couple at $E_{1/2}$ = +1.16 V which heralded the formation of a chemical product following the irreversible oxidation at +0.42 V. The IR spectrum of this complex (CH_2Cl_2 solution) had ν(C≡N) modes at 1955 (vs) and 1810 (sh) cm^{-1}, and its ^1H NMR spectrum (in CD_2Cl_2) displayed phenyl resonances at δ ~8.4 (br) and ~7.78 (m) and $-C_2H_4-$ resonances at δ 3.13 (d, J_{CH_2-P} = 20 Hz), the latter feature implying the presence of bidentate dppe. The most likely formulation for this unstable molecule is $Mo(CNPh)_4$(dppe), based upon an integration of the above signals in the ^1H NMR spectrum.

These reduction reactions are of interest from two points of view. First, they provide an alternative strategy to that already available[32] for the synthesis of mixed phosphine–isocyanide complexes of molybdenum(0).[33] Second, the metal-based reductions of $[M(CNR)_7]^{2+}$ and $[M(CNR)_{7-x}(PR_3)_x]^{2+}$ proceed by a different mechanism from that which occurs in the zinc reduction of $[Mo(CNCMe_3)_6I]^+$.[26,34] The latter reduction leads to the reductive coupling of two adjacent isocyanide ligands to afford the $[Mo(CNCMe_3)_4(Me_3CNHCCNHCMe_3)]^+$ cation.[26,34] The factors which govern the latter reaction course are currently under further study.[35]

Acknowledgment. We thank the National Science Foundation (Grant CHE79-09233) for research support and Mr. David E. Wigley for invaluable experimental assistance. We are also very grateful to Professor S. J. Lippard for providing us with a preprint of ref 24 and for keeping us informed of his research progress in this area.

Registry No. $Mo(CNPh)_6$, 14154-60-0; $W(CNPh)_6$, 14128-11-1; $[Mo(NO)(CNPh)_5]PF_6$, 78653-92-6; $[Mo(CNPh)_7](PF_6)_2$, 78653-88-0; $[Mo(CNPh)_6I]PF_6$, 79721-63-4; $[Mo(CNPh)_6I]BPh_4$, 79721-64-5; $[W(NO)(CNPh)_5]PF_6$, 78653-94-8; $[W(CNPh)_6I]BPh_4$, 79721-66-7; $[W(CNPh)_7](PF_6)_2$, 78653-90-4; $[Mo(CNPh)_6Cl]PF_6$, 79721-70-3; $[Mo(CNPh)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$, 79734-82-0; $[Mo(CNPh)_5(PEt_3)_2](PF_6)_2$, 79734-84-2; $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$, 79721-72-5; $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$, 79721-74-7; $[Mo(CNPh)_6(PPh_3)](PF_6)_2$, 79721-76-9; $[Mo(CNPh)_5(P(OEt)_3)_2](PF_6)_2$, 79721-78-1; $[Mo(CNPh)_5(dppe)](PF_6)_2$, 79721-80-5; $[Mo(CNPh)_5(dppm)](PF_6)_2$, 79734-86-4; $[W(CNPh)_5(PEt_3)_2](PF_6)_2$, 79721-82-7; $[W(CNPh)_5(PEtPh_2)_2](PF_6)_2$, 79721-84-9; $[W(CNPh)_6(PPh_3)](PF_6)_2$, 79721-86-1; $[W(CNPh)_5(dppe)](PF_6)_2$, 79721-88-3; $W_2(dmhp)_4$, 69351-88-8; $W_2(mhp)_4$, 67634-84-8.

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Synthesis of Cyclic Aminooxo- and Dioxocarbenes from Carbonyl Ligands in Complexes of Iron and Manganese

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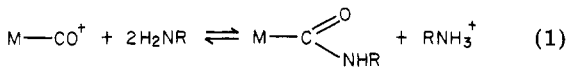
Received August 25, 1981

Electrophilic CO ligands in metal carbonyl complexes are converted to cyclic aminooxo- or dioxocarbene ligands by the following reactions: $M{-}C{\equiv}O^+ + H_3NCH_2CH_2Br^+ + 2B \rightarrow M{-}\overline{COCH_2CH_2NH}^+ + 2BH^+ + Br^-$; $M{-}C{\equiv}O^+ + HOCH_2CH_2Br + B \rightarrow M{-}\overline{COCH_2CH_2O}^+ + BH^+ + Br^-$. The base B used in these reactions is frequently NaH, but Et_3N and K_2CO_3 can also be successfully applied in certain cases. It is suggested that the reactions proceed by nucleophilic attack of the amine or alkoxide on a CO carbon atom to give a carbamoyl or alkoxycarbonyl intermediate, which cyclizes intramolecularly to yield the carbene products. One CO group in each of the following complexes has been observed to undergo one or both of these reactions: $FeCp(CO)_3^+$, $MnCp(NO)(CO)_2^+$, $MnCp(NO)(P(OPh)_3)(CO)^+$, $MnCp(NO)(CNC_6H_{11})(CO)^+$, and $Fe(CO)_5$. The reaction of $MnCp(NO)(CO)_2^+$ with $HOCH_2CH_2Br$ is the only one which leads to a dicarbene complex, $MnCp(NO)(\overline{COCH_2CH_2O})_2^+$. On the basis of studies of these and other metal carbonyl complexes, it appears that only CO groups that are sufficiently electropositive and have ν(CO) force constants equal to or greater than 17.0 mdyn/Å participate in these reactions. The amino group in $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$ is deprotonated by NaH or K_2CO_3 to give the imine complex $FeCp(CO)_2(\overline{COCH_2CH_2N})$ which reacts with $PdCl_2(NCMe)_2$ to yield the di-chloro-bridged dimer *sym,-trans*-$[FeCp(CO)_2(\overline{COCH_2CH_2N})Pd(\mu\text{-}Cl)Cl]_2$ in which the imine complexes are coordinated to the Pd(II) via their N atoms. Trends in the infrared and ^1H and ^{13}C NMR spectra of the complexes are discussed.

Introduction

Aliphatic amines react with electrophilic carbonyl ligands to give carbamoyl complexes (eq 1).[2,3] The reactivity



(1)

of a given CO ligand depends upon its electron density, which is reflected in its C–O stretching force constant.[4] Those CO ligands with force constants greater than approximately 17.2 mdyn/Å readily form carbamoyl com-

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
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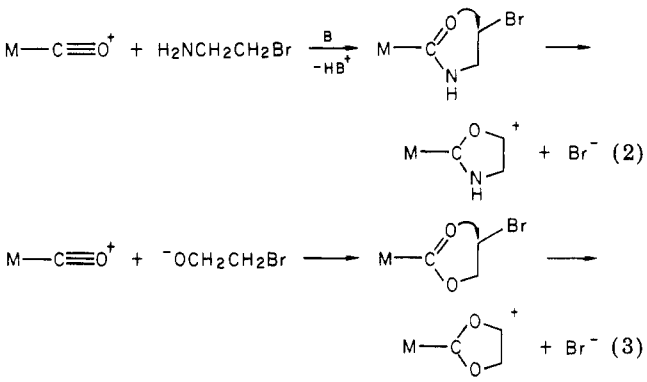
plexes; those with force constants between approximately 16.5 and 17.2 mdyn/Å give reversible equilibrium mixtures of carbonyl reactant and carbamoyl product; and those with constants below 16.5 mdyn/Å show no evidence of carbamoyl formation.[2] Alkoxide ions (RO^-) show a similar reactivity although they have not been studied in as great detail.

The present investigation was designed to take advantage of carbonyl ligand reactivity in the synthesis of cyclic carbene complexes. Using amines and alkoxides with a good leaving group in the β-position, it was hoped that cyclization to the carbene would occur. With (2-bromoethyl)amine (and base B) and 2-bromoethoxide, the reactions would occur as shown in eq 2 and 3. Previously,



Stone and co-workers[5] showed that $Mn(CO)_6^+$ reacts with $HOCH_2CH_2Cl$ in the presence of Et_3N to give the alkoxycarbonyl complex, $Mn(CO)_5[C(=O)OCH_2CH_2Cl]$, which upon treatment with Ag^+ cyclizes to give the dioxocarbene, $Mn(CO)_5[\overline{COCH_2CH_2O}]^+$. The cyclization did not occur without assistance from Ag^+. In the present study, cyclization occurs spontaneously in both reactions 2 and 3. The generality of these reactions is explored, and the spectroscopic properties of the carbene products are reported.

Experimental Section

General Methods. Unless otherwise noted, reagent chemicals of the highest quality available were used without further purification. All reactions were performed under an N_2 atmosphere. Except for that of $Fe(CO)_4(\overline{COCH_2CH_2NH})$, product isolations were carried out in air atmosphere. Infrared spectra were recorded on Perkin Elmer 281, Beckman 4250, or IBM 98 (Fourier Transform) instrument; ^1H- and ^{13}C-NMR spectra were recorded on a JEOL FX-90Q spectrometer.

Starting Complexes. $[FeCp(CO)_3]CF_3SO_3$[6] and $[MnCp(NO)(CO)_2]PF_6$[7] were prepared by literature methods.

$[MnCp(NO)(CO)(L)]PF_6$ (L = CNC_6H_{11}, $P(OPh)_3$). These complexes were prepared by a modification of the method of Brunner and Schindler.[8] A solution (~0.25 M) of $[MnCp(NO)(CO)_2]PF_6$ (0.5 mmol) in CH_3CN was reacted with a solution (~0.25 M) of L (0.5 mmol) in CH_3CN for 2 h at room temperature. Evaporation to dryness was followed by extraction with 10 mL of CH_2Cl_2 and filtration through Celite. The filtrate was concentrated to about 3 mL, and the product was crystallized by adding diethyl ether. Yields: 74% for L = CNC_6H_{11}; 88% for L = $P(OPh)_3$.

Synthesis of Complexes. $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$. To a suspension of 240 mg (1.17 mmol) of $[BrCH_2CH_2NH_3]Br$ in 20 mL of CH_3CN was added 100 mg (2.1 mmol) of 50% NaH in oil. After being stirred for 5 min, the mixture was treated with 400 mg (1.13 mmol) of $[FeCp(CO)_3]CF_3SO_3$ and stirred for an additional 15 min. An excess of KPF_6 (~2 g) was added to exchange the anion, and the mixture was stirred for 5 min. The solvent was removed under reduced pressure, and the residue was treated with several small portions of ether until the washings were colorless. The dried residue was extracted with CH_2Cl_2 and filtered through $MgSO_4$. The yellow filtrate was concentrated until pale yellow needles started to appear. Further crystallization was induced by the addition of ether: yield 290 mg (65.3%); mp 132 °C. Anal. Calcd for $C_{10}H_{10}F_6FeNO_3P$: C, 30.56; H, 2.56; N, 3.56. Found: C, 30.62; H, 2.54; N, 3.61.

$[FeCp(CO)_2(\overline{COCH_2CH_2O})]PF_6$. To 200 mg (0.564 mmol) of $[FeCp(CO)_3]CF_3SO_3$ was added 1.5 mL (21 mmol) of $BrCH_2CH_2OH$. To this stirred mixture was added ~150 mg (3.1 mmol) of 50% NaH in oil in small portions. Vigorous H_2 evolution was observed, and the reaction flask was cooled in an ice bath. After 5 min, excess $BrCH_2CH_2OH$ was removed under reduced pressure. The residue was treated with 10 mL of CH_3CN, and excess KPF_6 (~2 g) was added. Filtration through Celite resulted in a red filtrate. Removal of the solvent was followed by washing of the residue with ether until the washings became colorless. The residue was extracted with CH_2Cl_2 and filtered through $MgSO_4$. The filtrate was concentrated, and pale yellow crystals of the product precipitated upon addition of ether: yield 134 mg (60.3%); mp 129 °C. Anal. Calcd for $C_{10}H_9F_6FeO_4P$: C, 30.48; H, 2.30. Found: C, 30.40; H, 2.33.

$[MnCp(NO)(CO)(\overline{COCH_2CH_2NH})]PF_6$. The same procedure as for $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$ was used. Starting with 350 mg (~1 mmol) of $[MnCp(NO)(CO)_2]PF_6$, 280 mg (71%) of orange crystalline product was obtained; mp 134 °C. Anal. Calcd for $C_9H_{10}F_6MnN_2O_3P$: C, 27.43; H, 2.56; N, 7.10. Found: C, 27.58; H, 2.61; N, 7.06.

$[MnCp(NO)(\overline{COCH_2CH_2O})_2]PF_6$. The same procedure as for $[FeCp(CO)_2(\overline{COCH_2CH_2O})]PF_6$ was followed. Starting with 100 mg (0.285 mmol) of $[MnCp(NO)(CO)_2]PF_6$, the yield of product was 94 mg (75%). Yellow needles were obtained from CH_2Cl_2/ether and yellow-orange cubes from CH_3CN/ether; mp 232 °C. Anal. Calcd for $C_{11}H_{13}F_6MnNO_5P$: C, 30.09; H, 2.98; N, 3.19. Found: C, 30.09; H, 2.99; N, 3.12.

$[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2NH})]PF_6$. Following the procedure for the preparation of $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$ and starting with 300 mg (0.474 mmol) of $[MnCp(NO)(CO)(P(OPh)_3)]PF_6$, 230 mg (72%) of the orange crystalline product was isolated; mp 64 °C. Anal. Calcd for $C_{26}H_{25}F_6MnN_2O_5P_2$: C, 46.17; H, 3.73; N, 4.14. Found: C, 46.05; H, 3.90; N, 4.05.

$[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})]PF_6$. To 100 mg (0.158 mmol) of $[MnCp(NO)(CO)(P(OPh)_3)]PF_6$ dissolved in 4 mL of CH_2Cl_2 was added 40 mg (0.32 mmol) of $BrCH_2CH_2OH$ and an excess of 50% NaH in oil. The reaction was followed in the IR, and a shift of the ν(NO) band and the simultaneous disappearance of the ν(CO) band were observed after 1 h. The resulting suspension was filtered and washed with CH_2Cl_2 through Celite. Upon removal of CH_2Cl_2 under vacuum, a yellow-orange oil resulted. The oil was washed with dry ether and stirred with hexanes; it slowly converted to a yellow powder; yield 61 mg (57%). Anal. Calcd for $C_{26}H_{24}F_6MnNO_6P_2$: C, 46.10; H, 3.57; N, 2.07. Found: C, 46.15; H, 3.60; N, 2.00.

$[MnCp(NO)(CNC_6H_{11})(\overline{COCH_2CH_2O})]PF_6$. Using the same procedure as for the preparation of $[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})]PF_6$ and starting with 50 mg of $[MnCp(NO)(CO)CNC_6H_{11})]PF_6$ and using a reaction time of 22 h, we isolated 50 mg (90%) of the product as a red-orange viscous oil at 25 °C; it solidified at about −20 °C. Anal. Calcd for $C_{15}H_{20}F_6MnN_2O_3P$: C, 37.83; H, 4.23; N, 5.88. Found: C, 38.43; H, 4.42; N, 6.07.

$Fe(CO)_4(\overline{COCH_2CH_2NH})$. To 305 mg (1.49 mmol) of finely ground $[BrCH_2CH_2NH_3]Br$ was added 3 mL of NEt_3 in a Schlenk tube. Following repeated evacuation and saturation with N_2 of the solution, 0.20 mL (1.49 mmol) of $Fe(CO)_5$ (toxic!) was added with a syringe. The mixture was stirred for about 2 h under N_2 at 25 °C. This was followed by distillation under vacuum at room

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(8) Brunner, H.; Schindler, H.-D. *J. Organomet. Chem.* **1969**, *19*, 135.

temperature of all NEt_3 and the small amount of unreacted $Fe(CO)_5$. The residue was treated with 25 mL of CaH_2–dried ether and the mixture stirred for 5 min. The resulting suspension was filtered through Celite into a connected Schlenk tube. All these manipulations were carried out in a closed system under an N_2 atmosphere. The pale yellow filtrate was concentrated until all ether was removed and a bright yellow oil resulted; yield 310 mg (87%). The compound is very air sensitive. Opening the Schlenk tube even under a stream of N_2 causes the color to change to orange within seconds. It was characterized by its infrared and ^1H and ^{13}C NMR spectra.

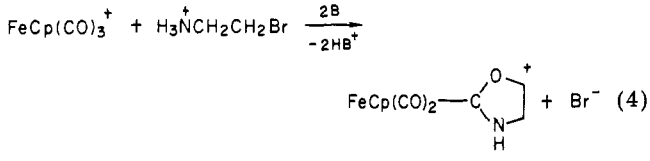
Deprotonation of $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$. Method A. Finely ground K_2CO_3 (~500 mg, ~4.5 mmol) was added to a mixture of 100 mg (0.254 mmol) of $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$ in 3 mL of CH_2Cl_2. After 1–2 days, an intensely yellow solution had formed together with a reddish brown precipitate. Removal under vacuum of CH_2Cl_2 was followed by extraction with ~20 mL of dry ether; the resulting suspension was filtered under $MgSO_4$. After the filtrate was evaporated to dryness, a yellow amorphous powder of $FeCp(CO)_2(\overline{COCH_2CH_2N})$ remained (~30 mg, 48%). The compound was extremely moisture sensitive and very soluble in common organic solvents. If opened to the atmosphere, it turned red and darkened within a few hours. In dilute solution (CH_2Cl_2, ether, hexanes) it can be kept for several hours without noticeable decomposition, whereas, in very concentrated solution, the formation of a red brown precipitate was observed in 4 h.

Method B. The yellow compound was also obtained by treating $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$ in CH_2Cl_2 with a large excess of 50% NaH in oil. After 2–3 h, the product was isolated together with some of the oil (from the NaH) which stabilized the complex.

$[FeCp(CO)_2(\overline{COCH_2CH_2N})PdCl(\mu\text{-}Cl)]_2$. A fresh sample of $FeCp(CO)_2(\overline{COCH_2CH_2N})$ prepared from 100 mg (0.254 mmol) of $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$ (method B) was dissolved in ~5 mL of CH_2Cl_2 to which 66 mg (0.255 mmol) of $PdCl_2(CH_3CN)_2$ was added. While the solution stirred for 30 min at 25 °C, its color turned orange-red and some brown precipitate formed. The suspension was filtered over $MgSO_4$, and the product was isolated as a brown-orange powder (30 mg, 28%) by concentration of the filtrate and addition of ether. It decomposed as a solid at 126 °C (turns black). The compound is moderately soluble in CH_2Cl_2 and CH_3CN, slightly soluble in ether, and insoluble in hexanes. In solution it is unstable and shows the same type of decomposition as $FeCp(CO)_2(\overline{COCH_2CH_2N})$. Anal. Calcd for $C_{20}H_{18}Cl_4Fe_2N_2O_6Pd_2$: C, 28.31; H, 2.14; N, 3.30. Found: C, 27.98; H, 2.23; N, 3.36.

Results and Discussion

Reactions of $FeCp(CO)_3^+$. This cation is known[9] to react with aliphatic amines and alkoxides to give carbamoyl and alkoxycarbonyl complexes. When $FeCp(CO)_3^+$ is added to a mixture of $H_3NCH_2CH_2Br^+$ and NaH, a CO group is rapidly converted to a carbene in 65% yield.



(4)

The metal complex cation is added last to the reaction mixture in order to avoid its reaction with the CH_3CN solvent. The most convenient base for this reaction is NaH in mineral oil, which presumably gives H_2 as the other product. However, the reaction also proceeds, but in lower yields, with K_2CO_3 and Et_3N in CH_2Cl_2 solvent. Some $[CpFe(CO)_2]_2$ is also formed as a byproduct in these reactions. There is no infrared evidence during the course of the reaction for a carbamoyl intermediate; it presumably cyclizes rapidly to the carbene ligand under the reaction conditions. Even in the presence of excess $H_3NCH_2CH_2Br^+$ and base, the conversion of a second CO ligand to a carbene does not occur. The lack of further reaction of $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$ is presumably due to the higher electron density on the CO carbons, as indicated by the ν(CO) force constant (16.76 mdyn/Å, Table I), which inhibits attack by an amine.

Treatment of $FeCp(CO)_3^+$ in liquid $HOCH_2CH_2Br$ with NaH rapidly gives the dioxocarbene in 60% yield.

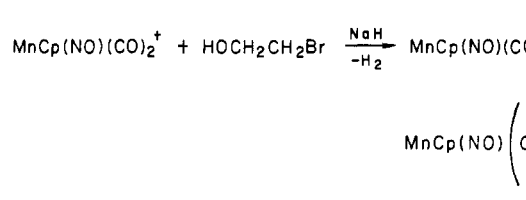
(5)

There is no IR evidence for the presumed (eq 3) alkoxycarbonyl intermediate.

These aminooxo- and dioxocarbene complexes, as well as those described below, are characterized by their elemental analyses and infrared (Table I) and ^1H (Table II) and ^{13}C (Table III) NMR spectra. Except where indicated otherwise, all are stable in air for weeks in the solid state.

Reactions of $MnCp(NO)(CO)_2^+$. The known[10] reaction of $MnCp(NO)(CO)_2^+$ with aliphatic amines to give carbamoyl complexes suggests that one CO group in $MnCp(NO)(CO)_2^+$ could be converted to an aminooxocarbene upon reaction with $H_3NCH_2CH_2Br^+$ and base. Indeed, the carbene $MnCp(NO)(CO)(\overline{COCH_2CH_2NH})^+$ is isolated in 71% yield in this reaction when NaH is the base. An excess of base should be avoided because the carbene product is decomposed by strong bases (the same is true for $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$, vide infra). An excess of $H_3NCH_2CH_2Br^+$ and NaH does not give the dicarbene complex.

The cationic complex $MnCp(NO)(CO)_2^+$ has been reported[11] to react with methoxide ion to give the alkoxycarbonyl $MnCp(NO)(CO)(CO_2Me)$. The reaction of $MnCp(NO)(CO)_2^+$ with 2-bromoethanol and NaH gives a mixture of carbene products.



(6)

It appears that the dicarbene complex $MnCp(NO)(\overline{COCH_2CH_2O})_2^+$ is formed from the monocarbene by conversion of the last CO group into a carbene. Even using only 1 mol of $HOCH_2CH_2Br$/mol of $MnCp(NO)(CO)_2^+$ gave more dicarbene than monocarbene complex. This probably is due to the low solubility of the starting complex as compared to the monocarbene which could undergo the second reaction more readily. For this reason the monocarbene complex was not isolated in a pure form. The pure dicarbene was isolated from reactions in which $HOCH_2CH_2Br$ was used as the solvent.

That the CO in $MnCp(NO)(CO)(\overline{COCH_2CH_2O})^+$ is also converted into a carbene may be understood in terms

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Table I. Infrared Frequencies Measured in CH_2Cl_2 Solvent

complex	ν(CO), cm^{-1}	k(CO)[a]	ν(NO), cm^{-1}	k(NO)[a]
$[FeCp(CO)_3]CF_3SO_3$	2120, 2065	17.60		
$[FeCp(CO)_2(COCH_2CH_2NH)]PF_6$	2060 s, 2015 s	16.76		
$FeCp(CO)_2(COCH_2CH_2N)$	2035 s, 1980 s	16.27		
$[FeCp(CO)_2(COCH_2CH_2N)PdCl(\mu\text{-}Cl)]_2$[b]	2043 s, 1996 s	16.47		
$[FeCp(CO)_2(COCH_2CH_2O)]PF_6$	2080 s, 2035 s	17.09		
$[MnCp(NO)(CO)_2]PF_6$	2125, 2075	17.80	1840	14.89
$[MnCp(NO)(CO)(COCH_2CH_2NH)]PF_6$	2047	16.92	1805	14.33
$[MnCp(NO)(CO)(COCH_2CH_2O)]^+$	2060	17.14	1820	14.57
$[MnCp(NO)(COCH_2CH_2O)_2]PF_6$			1790	14.09
$[MnCp(NO)(CO)(CNC_6H_{11})]PF_6$[c]	2060	17.14	1823	14.61
$[MnCp(NO)(CNC_6H_{11})(COCH_2CH_2O)]PF_6$[d]			1790	14.09
$[MnCp(NO)(P(OPh)_3)(CO)]PF_6$	2060	17.14	1827	14.68
$[MnCp(NO)(P(OPh)_3)(COCH_2CH_2NH)]PF_6$			1775	13.85
$[MnCp(NO)(P(OPh)_3)(COCH_2CH_2O)]PF_6$			1795	14.17
$Fe(CO)_5$	2000, 2023	17.0 ax 16.4 eq		
$Fe(CO)_4(COCH_2CH_2NH)$	2050 w, 2040 w, 1970 s, 1950 s, 1935 sh			

[a] mdyn/A. [b] In Nujol mull: ν(CO) at 2031 s, 1976 s cm^{-1}; ν(Pd-Cl) at 319 m, 336 s, 357 m cm^{-1}. In CsCl pellet: ν(CO) at 2038 s, 1984 s cm^{-1}; ν(Pd-Cl) at 330 s, 361 m cm^{-1}. [c] ν(CN) at 2210 cm^{-1}. [d] ν(CN) at 2190 cm^{-1}.

Table II. ^{1}H NMR Data[a]

complex	OCH_2	$NHCH_2$	NH	Cp
$[FeCp(CO)_2(COCH_2CH_2NH)]PF_6$[b]	4.60[c]	3.70[c]	9.5	5.30
$FeCp(CO)_2(COCH_2CH_2N)$[b]	3.75[c]	3.60[c]		5.00
$[FeCp(CO)_2(COCH_2CH_2N)PdCl(\mu\text{-}Cl)]_2$[b]	4.05[c]	3.59[c]		5.40
$[FeCp(CO)_2(COCH_2CH_2O)]PF_6$[b]	4.73			5.38
$[MnCp(NO)(CO)_2]PF_6$[d]				6.14
$[MnCp(NO)(CO)(COCH_2CH_2NH)]PF_6$[b]	4.62[c]	3.71[c]	9.1	5.44
$[MnCp(NO)(CO)(COCH_2CH_2O)]^+$[d]	5.13			5.95
$[MnCp(NO)(COCH_2CH_2O)_2]PF_6$[b]	4.65			5.35
	4.92[d]			5.60[d]
$[MnCp(NO)(CO)(CNC_6H_{11})]PF_6$[d]				5.88[e]
$[MnCp(NO)(CNC_6H_{11})(COCH_2CH_2O)]PF_6$[b]	4.71			5.35
$[MnCp(NO)(P(OPh)_3)(CO)]PF_6$[d]				5.67[e]
$[MnCp(NO)(P(OPh)_3)(COCH_2CH_2NH)]PF_6$[b]	4.40[c]	3.50[c]	8.7	4.90
$[MnCp(NO)(P(OPh)_3)(COCH_2CH_2O)]PF_6$[b]	4.55			5.00
$[Fe(CO)_4(COCH_2CH_2NH)]$[f]	3.19[c]	1.97[c]	5.96	

[a] Chemical shifts (δ) in parts per million downfield from tetramethylsilane. [b] In CD_3CN solvent. [c] See text for discussion of AA'BB' splitting of these protons. [d] In acetone-d_6 solvent. [e] Reference 8. [f] In C_6D_6 solvent.

of its relatively high ν(CO) force constant (17.14 mdyn/Å). In this system, the dioxocarbene ligand is not sufficiently electron donating to prevent alkoxide attack at the remaining CO group.

Reactions of $MnCp(NO)(L)(CO)^+$. The phosphite complex $MnCp(NO)(P(OPh)_3)(CO)^+$ reacts with $H_3NCH_2CH_2Br^+$ and NaH in CH_3CN at room temperature to give a 72% yield of the aminooxocarbene

Table III. ^{13}C NMR Data[a]

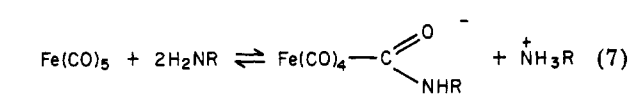
complex	C[b]	CO	OCH_2	$NHCH_2$	Cp
$[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$[c]	221.5	212.1	74.2	47.0	88.7
	221.5[d]	212.5[d]	74.2[d]	47.0[d]	88.7[d]
$FeCp(CO)_2(\overline{COCH_2CH_2N})$[e]	183.7[f]	214.3	64.9	56.2	85.6
	[g]	[g]	66.5[c]	57.3[c]	88.0[c]
$[FeCp(CO)_2(COCH_2CH_2N)PdCl(\mu\text{-}Cl)]_2$[e]	193.6[f]	212.5	67.0	56.0	86.2
$[FeCp(CO)_2(\overline{COCH_2CH_2O})]PF_6$[c]	243.4	210.5	74.8		89.9
$[MnCp(NO)(CO)(\overline{COCH_2CH_2NH})]PF_6$[c]	224.2[h]	229.4	74.4	46.9	96.2
$[MnCp(NO)(\overline{COCH_2CH_2O})_2]PF_6$[c]	263.0		73.5		96.9
$[MnCp(NO)(CNC_6H_{11})(\overline{COCH_2CH_2O})]PF_6$[c]	[g]		73.9		96.1
$[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2NH})]PF_6$[c]	239.7[i]		73.6	46.6	94.9
$[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})]PF_6$[c]	263.6[j]		73.9		95.7
$Fe(CO)_4(\overline{COCH_2CH_2NH})$[e]	233.1	216.0	71.3	44.9	
$Fe(CO)_4(\overline{CNRCH_2CH_2NR})$[k]	213.2	217.4			
$Fe(CO)_4(\overline{COCR_2CR_2O})$[k]	251.2	215.3			

[a] Chemical shifts in parts per million downfield from Me_4Si. [b] Carbene C atom. [c] In CD_3CN solvent. [d] In 3 M HCl/D_2O. [e] In C_6D_6 solvent. [f] Uncertain assignment due to low signal to noise. [g] Not observed. [h] Assignment based on line broadening due to ^{14}N quadrupolar coupling. [i] d, $J(PMnC) = 44.4$ Hz. [j] d, $J(PMnC) = 40.0$ Hz. [k] Reference 16.

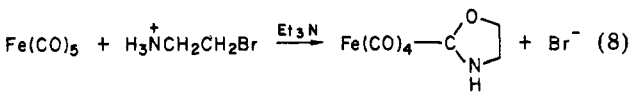
$MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2NH})^+$. The reaction of $MnCp(NO)(P(OPh)_3)(CO)^+$ with $HOCH_2CH_2Br$ and NaH gives the analogous dioxocarbene $MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})^+$ in 57% yield.

Since it is known[12] that certain isocyanide ligands undergo nucleophilic attack by alcohols and amines, a complex with both CO and CNR ligands was studied. The reaction of $MnCp(NO)(C{\equiv}N{-}C_6H_{11})(CO)^+$ with $HOCH_2CH_2Br$ and NaH leads exclusively to the dioxocarbene product $MnCp(NO)(CNC_6H_{11})(\overline{COCH_2CH_2O})^+$ in 90% yield.

Reaction of $Fe(CO)_5$. Pentacarbonyliron reacts with primary and secondary amines according to eq 7.[13,14] The



equilibrium lies to the right in polar solvents and to the left in nonpolar solvents. That carbamoyl formation occurs suggests that $Fe(CO)_5$ would yield an aminooxocarbene. Indeed, such a reaction does occur at 25 °C when Et_3N is used as the base and the solvent.



The very air-sensitive carbene product does not form when K_2CO_3 is the base and the solvent is either CH_2Cl_2 or tetrahydrofuran (THF).

Acyclic aminooxocarbene complexes, e.g., $Fe(CO)_4[C(OEt)(NMe_2)]$,[15,16] have been prepared previously and have $\nu(CO)$ absorptions very similar to those (Table I) of the cyclic carbene complex reported here. As for the acyclic carbenes, the number and intensity of the $\nu(CO)$ bands do not allow one to assign unambiguously the carbene ligand to an axial or equatorial position in the $Fe(CO)_4(\overline{COCH_2CH_2NH})$ molecule. The equivalence of all four CO groups in the ^{13}C NMR spectrum (Table III) indicates that it is fluxional at room temperature.

Although cyclic dioxocarbene complexes $Fe(CO)_4(\overline{COCR_2CR_2O})$ have been reported,[17] there was no evidence for the formation of $Fe(CO)_4(\overline{COCH_2CH_2O})$ in reactions of $Fe(CO)_5$ with $HOCH_2CH_2Br$ and the bases K_2CO_3 or NaH.

Trends in Reactivity. Those metal carbonyl complexes which have been converted to aminooxocarbenes and/or dioxocarbenes as in eq 2 and 3 are as follows (their $\nu(CO)$ force constants are given in parentheses, see Table I): $MnCp(NO)(CO)_2^+$ (17.80 mdyn/Å), $FeCp(CO)_3^+$ (17.60), $MnCp(NO)(CO)(CNC_6H_{11})^+$ (17.14), $MnCp(NO)(CO)(P(OPh)_3)^+$ (17.14), $MnCp(NO)(CO)(\overline{COCH_2CH_2O})^+$ (17.14), and $Fe(CO)_5$ (17.0 axial, 16.4 equatorial). The $M(CO)_6$ complexes (M = Cr (16.49 mdyn/Å), Mo (16.52), or W (16.41)) did not yield carbenes; they are also known not to form carbamoyl complexes with amines. Likewise, $MnCp(CO)_3$ (15.6 mdyn/Å) did not react, and it is known[18] not to form carbamoyl complexes.

These results suggest that the tendency of a CO group to react according to eq 2 and 3 follows its ability to react with amines to give carbamoyl complexes. It appears that CO ligands with $\nu(CO)$ force constants equal to or greater than 17.0 mdyn/Å are likely to be converted into carbenes; those below 17.0 mdyn/Å are unlikely to react in this manner. That no reactions are observed for force constants below 17.0 mdyn/Å suggests that $H_2NCH_2CH_2Br$ is somewhat less reactive than primary aliphatic amines.

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This is understandable in view of the lower basicity (and probably nucleophilicity) of $H_2NCH_2CH_2Br$ ($pK_a \approx 8.49$)[19] as compared to that ($pK_a \approx 10.5$) for primary aliphatic amines. While other factors such as steric considerations and CO lability may affect carbene formation in specific complexes, the force constant appears to be a useful guideline for estimating reactivity.

Even though the general reactivity of $H_2NCH_2CH_2Br$ is consistent with its reaction according to eq 2, it should be noted that $H_2NCH_2CH_2Br$ cyclizes[20] readily to aziridine under conditions similar to those used in the reactions. Thus, some aziridine is likely to be present in the reaction solutions, and aziridine could be involved in the carbene formation. This possibility is being investigated.

In the reactions reported above, the 5-membered carbene ligand is formed. Attempts to generate 6-membered carbene ligands from $FeCp(CO)_3^+$ and $MnCp(NO)(CO)_2^+$ using $NH_3CH_2CH_2CH_2Br^+$ or $HOCH_2CH_2CH_2Br$ under the same conditions used to form the 5-membered carbenes gave no carbene formation. It appears that ring closure to the 6-membered carbene is less favorable.

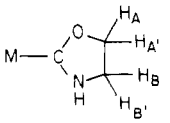
Certain coordinated isocyanide ligands have been observed to undergo nucleophilic attack by amines and alcohols.[12] Some evidence[21] indicates that these reactions are slower than those occurring with CO groups, which may account for the conversion of only the CO group of $MnCp(NO)(CO)(CNC_6H_{11})^+$ to a carbene. However, we also did not observe the formation of carbene complexes in reactions of $H_3NCH_2CH_2Br^+$ or $HOCH_2CH_2Br$ with $MnCp(NO)(CNC_6H_{11})_2^+$ or *cis*-$PtCl_2(P(OPh)_3)(CNC_6H_{11})$. It is perhaps worth exploring these reactions further by using less bulky isocyanide ligands.

Spectroscopic Properties of the Carbene Complexes. Infrared Spectra. With ν(CO) force constants as a measure of the donor–acceptor properties of L in the $FeCp(CO)_2(L)^+$ complexes, it is evident (Table I) that the π-acceptor/σ-donor ratio of L decreases in the order (k-(CO) in parentheses): CO (17.60 mdyn/Å) > $\overline{COCH_2CH_2O}$ (17.09) > $\overline{COCH_2CH_2NH}$ (16.76). The same trend is found in the ν(CO) and ν(NO) force constants of the $MnCp(NO)(CO)(L)^+$ series of complexes. The stronger π-bonding ability of the nitrogen or its lower electronegativity as compared to those of oxygen accounts for the aminooxocarbene being a better donor ligand than the dioxocarbene.[22]

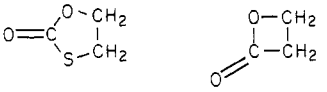
The π-acceptor/σ-donor ratio of both carbene ligands is clearly lower than that of CO. By comparing ν(CO) and ν(NO) force constants of the $MnCp(NO)(CO)L^+$ complexes, one can observe that the dioxocarbene ligand, $-\overline{COCH_2CH_2O}$ has electronic properties similar to those of $P(OPh)_3$ and $C{\equiv}N{-}C_6H_{11}$. Force constants (ν(CO)) of the $FeCp(CO)_2L^+$ complexes indicate that the aminooxocarbene ligand, $-\overline{COCH_2CH_2NH}$, has electronic properties similar to those of the dithiocarbene, $-C(SMe)_2$, and to PPh_3.[22]

^{1}H NMR Spectra. The ^{1}H NMR spectra (Table II) of all of the dioxocarbene ($-\overline{COCH_2CH_2O}$) complexes show a singlet for the carbene protons in the range δ 4.5–5.2. In the complexes $MnCp(NO)(L)(\overline{COCH_2CH_2O})^+$, the lowest field carbene resonance occurs for L = CO (δ 5.13), whereas those complexes with more strongly electron donating ligands (CNC_6H_{11}, $P(OPh)_3$, and $-\overline{COCH_2CH_2O}$) have resonances at higher field in the region of δ 4.55–4.71.

^{1}H NMR spectra of the aminooxocarbene complexes are somewhat more complicated. Although they appear to be close to that expected for an A_2B_2 spin system, they really represent AA′BB′ systems.



The AA′BB′ systems have been analyzed in detail in related organic ring systems such as:[23]



On the basis of assignments of protons in 2-oxazolines and related systems,[24,25] the methylene protons adjacent to the oxygen are assigned to the lower field resonances which are approximately 1-ppm downfield from those of the methylene protons adjacent to the nitrogen.

As for the dioxocarbene complexes, the methylene resonances of $MnCp(NO)(CO)(\overline{COCH_2CH_2NH})^+$ (δ 4.62, 3.71) are downfield from those in the electron-rich $MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2NH})^+$ (δ 4.40, 3.50). The most upfield methylene resonances occur in the neutral complex $Fe(CO)_4(\overline{COCH_2CH_2NH})$ (δ 3.19, 1.97).

^{13}C NMR Spectra. The carbene carbon chemical shifts of the $-\overline{COCH_2CH_2NH}$ ligands occur in the range of 220–240 ppm, while those of the $-\overline{COCH_2CH_2O}$ occur at 240–263 ppm. In the acyclic carbene complexes $FeCp(CO)_2[C(XR)(YR)]^+$,[26] where X and Y = O, NH, S and/or Se, the carbene carbon chemical shifts depend upon the atoms bound to that carbon: $-C(NHR)_2$, 190–220 ppm; $-C(NHR)(OR)$, 220–230; $-C(OR)_2$, ~250; $-C(OR)(SR)$, $-C(SR)_2$, 280–310; $-C(SR)(SeR)$, ~320. The cyclic carbene complexes reported here also follow this trend. For example, in the $FeCp(CO)_2(carbene)^+$ and $Fe(CO)_4(carbene)$ complexes, the carbene carbon resonance of the $-\overline{COCH_2CH_2NH}$ compound is at approximately 20 ppm higher field than that of the analogous $-\overline{COCH_2CH_2O}$ compound. For the diaminocarbene $Fe(CO)_4(\overline{CNRCH_2CH_2NR})$[16] the carbene resonance (Table III) is 20 ppm still higher. The upfield shift caused by the nitrogen has been attributed to more π bonding in the C(carbene)–N bond than in the C(carbene)–O bond.[27] However, the difference between –OR and –NHR substituent effects in aliphatic hydrocarbons is also about 20 ppm.[25]

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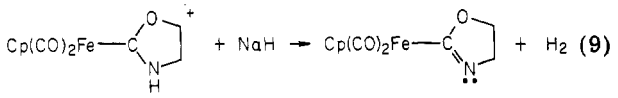
Replacement of the CO in $MnCp(NO)(CO)(\overline{COCH_2CH_2NH})^+$ by $P(OPh)_3$ shifts the carbene resonance downfield from 224.2 to 239.7 ppm; a similar trend was observed for the $FeCp(CO)(L)[C(SMe)_2]^+$ carbene carbon.[22] The carbene resonance is essentially the same (~263 ppm) for both $MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})^+$ and $MnCp(NO)(\overline{COCH_2CH_2O})_2^+$, which suggests that $P(OPh)_3$ and $-\overline{COCH_2CH_2O}$ have similar electronic properties, a conclusion that was also inferred from ν(CO) frequencies of the $MnCp(NO)(CO)(L)^+$ complexes.

Generation and Reactions of $FeCp(CO)_2(\overline{COCH_2CH_2N})$. This neutral imine complex can be produced by deprotonation of the aminooxocarbene in CH_2Cl_2 with K_2CO_3 or NaH.



It is also generated as a small amount of side product in the synthesis of the carbene (eq 4). Its instability, which prevented its isolation as a pure compound, contrasts with the high stability of its precursor carbene. As expected for a deprotonation, the ν(CO) frequencies (2060, 2015 cm^{-1}) of the carbene decrease to 2035 and 1980 cm^{-1} in $FeCp(CO)_2(\overline{COCH_2CH_2N})$. In ^1H NMR studies, deprotonation causes a shift of the OCH_2 and NCH_2 protons from δ 4.60 and 3.70, respectively, in the carbene to δ 3.75 and 3.60 in the imine. While an upfield shift of these protons is expected, the greater shift of the OCH_2 protons is surprising inasmuch as the deprotonation occurred at the nitrogen. In ^{13}C NMR studies, the OCH_2 carbon of the carbene shifts upfield upon deprotonation from 74.2 to 64.9 ppm, while the NCH_2 carbon shifts downfield from 47.0 to 56.2 ppm.

The imine complex $FeCp(CO)_2(\overline{COCH_2CH_2N})$ can be dissolved in 3 M aqueous HCl, where it is protonated to give the carbene, which is stable in the solution for at least 3 weeks. The HCl does not cleave the Fe–C bond. In pure water the imine decomposes rapidly. The basicity of the imine nitrogen is demonstrated by its reaction with $NH_4^+PF_6^-$ in CH_2Cl_2 at −70 °C to give the carbene.

The coordinating ability of the imine nitrogen is seen in its reaction with $PdCl_2(NCMe)_2$.

$$2FeCp(CO)_2(\overline{COCH_2CH_2N}) + 2PdCl_2(NCMe)_2 \xrightarrow{25\ °C} sym,trans\text{-}[FeCp(CO)_2(\overline{COCH_2CH_2N})Pd(\mu\text{-}Cl)Cl]_2 \quad (10)$$

The product is formulated as a di-μ-Cl bridged sym,trans dimer based on elemental analyses and the three ν(Pd–Cl) absorptions at 319, 336, and 357 cm^{-1} in the infrared region.[28] The ν(CO) frequencies of the compound (Table I) occur between those of $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$ and $FeCp(CO)_2(\overline{COCH_2CH_2N})$, which indicates that the Pd(II) is a weaker Lewis acid toward the imine nitrogen than H^+. In fact, the dimer reacts within a few minutes with gaseous HCl bubbled into a CH_2Cl_2 solution of the dimer to protonate the imine and to give the carbene $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$ and $PdCl_4^{2-}$.

Acknowledgment. Partial funding for the JEOL FX-90Q NMR spectrometer was provided by an instrumentation grant from the National Science Foundation.

Registry No. $[FeCp(CO)_2(\overline{COCH_2CH_2NH})]PF_6$, 69532-52-1; $FeCp(CO)_2(\overline{COCH_2CH_2N})$, 79664-06-5; $[FeCp(CO)_2(\overline{COCH_2CH_2N})PdCl(\mu\text{-}Cl)]_2$, 79664-07-6; $[FeCp(CO)_2(\overline{COCH_2CH_2O})]PF_6$, 79664-09-8; $[MnCp(NO)(CO)(\overline{COCH_2CH_2NH})]PF_6$, 79664-11-2; $[MnCp(NO)(CO)(\overline{COCH_2CH_2O}]^+$, 79664-12-3; $[MnCp(NO)(\overline{COCH_2CH_2O})_2]PF_6$, 79664-14-5; $[MnCp(NO)(CO)(CNC_6H_{11})]PF_6$, 32982-02-8; $[MnCp(NO)(CNC_6H_{11})(\overline{COCH_2CH_2O})]PF_6$, 79664-16-7; $[MnCp(NO)(P(OPh)^3)(CO)]PF_6$, 32875-46-0; $[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2NH})]PF_6$, 79680-93-6; $[MnCp(NO)(P(OPh)_3)(\overline{COCH_2CH_2O})]PF_6$, 79664-18-9; $Fe(CO)_4(\overline{COCH_2CH_2NH})$, 79664-19-0; $[FeCp(CO)_3]CF_3SO_3$, 76136-47-5; $[MnCp(NO)(CO)_2]PF_6$, 31921-90-1.

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