solvent-assisted pentacoordinate intermediate for the reasons mentioned above and because of the similarity to the process shown in eq 3, where L might be a solvent molecule.

There are two possible explanations for the second-order term. The mechanism might involve a bimolecular interaction to form a five-coordinate rhodium dimer such as III which might either undergo an intramolecu-
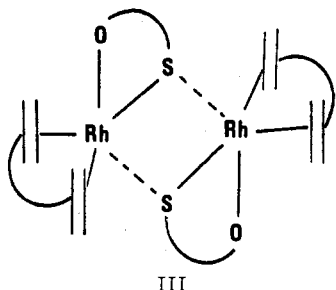
III

lar rearrangement or exchange monothio-β-diketonate ligands. Such a mechanism has been proposed for the second-order rate law observed for compounds of the type (diene)RhLCl in the absence of added ligand.[25] The second possibility is that, despite efforts to purify the complex, an impurity or decomposition product is present in the solid which acts as an added ligand in solution. The low value of the second-order rate constant, compared to the values obtained in the presence of a strong nucleophile (Table III),[32] and the nonreproducibility (mentioned previously) in measuring this constant support this explanation.

(32) Assuming an activation energy of 17 kcal/mol, an impurity with a basicity comparable to that of triphenylarsine would have to be present only to the extent of ~0.02% of the (NOR)Rh(SDBM) concentration to account for the observed k_2 of 37 M^{-1} sec^{-1} at 74°.

In the absence of additional evidence, some insight into the principal type of mechanism involved in the exchange can be derived from the observed differences in rate for different olefins. The observed ordering of rates NOR ≫ TBQ ≫ COD in the absence of added ligand is the same as the second-order rate constants in the presence of added triphenylarsine (Table III).[33] From this result it is likely that a fluxional five-coordinate species is the major intermediate for the site exchange where the fifth ligand might be provided by the solvent, an impurity, or another molecule of complex.

In conclusion it may be noted that the fluxional behavior of the (diolefin)Rh(SDBM) compounds studied here is similar to previously studied systems[2,3] in several respects. First, involvement of a five-coordinate intermediate, or transition state, is indicated. Second, faster exchange rates for norbornadiene compared to cycloocta-1,5-diene complexes have been demonstrated. Finally, the independence of intramolecular rearrangements and intermolecular exchange is confirmed, the latter process being greatly suppressed if not eliminated by the use of chelating ligands in compounds of types I and II.

(33) The second-order rate constants can be compared despite systematic errors[22] in calculating the exchange rates of (NOR)Rh(SDBM) and (COD)-Rh(SDBM). The application of a 50% maximum error (calculated in a related system in which H_a–H_b coupling is neglected[21]) does not affect the relative ordering of the rate constants.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA, AND MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

Metal Carbonyl Complexes of Cyclic Azines. I. Reactions of Fe₂(CO)₉, Ru₃(CO)₁₂, and [Rh(CO)₂Cl]₂ with 3,5,7-Triphenyl-4H-1,2-diazepine and 3,5,7-Triphenyl-4,5,6-trihydro-1,2-diazepine

BY D. P. MADDEN,[1a] A. J. CARTY,*[1a] AND T. BIRCHALL[1b]

3,5,7-Triphenyl-4H-1,2-diazepine reacts with Fe₂(CO)₉ to yield a nitrogen-bridged complex (C₂₃H₁₈N₂)Fe₂(CO)₆ lacking an N–N bond and with two nonequivalent iron atoms. The nuclear magnetic resonance, mass and Mössbauer spectra of this compound are discussed in the light of the X-ray molecular structure. An analogous complex, (C₂₃H₂₀N₂)Fe₂(CO)₆, is the product obtained from 3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine and Fe₂(CO)₉. By contrast [Rh(CO)₂X]₂ (X = Cl, Br) yield square-planar complexes of the types (C₂₃H₁₈N₂)Rh(CO)₂X (X = Cl, Br) and (C₂₃H₂₀N₂)[Rh(CO)₂X]₂ (X = Cl, Br) with these azines. In the former compounds the heterocyclic azine is bonded to rhodium *via* a nitrogen atom, the N–N bond being retained. In the latter the diazepine behaves as a bridging ligand using both nitrogen atoms as donors. The nuclear magnetic resonance spectrum of (C₂₃H₁₈N₂)Rh(CO)₂Cl indicates that the conformation of the seven-membered ring is identical in the complex and the free ligand. Reactions of these azines with Ru₃(CO)₁₂ are also described.

Introduction

The reactions of metal carbonyl derivatives with olefinic ligands have provided a diverse variety of organometallic π complexes.[2] By contrast few studies have been reported on the coordination properties of ligands

containing the azine chromophore >C=N—N=C<. From the reaction of benzalazine with diiron enneacarbonyl, Otsuka and coworkers[3a] isolated a derivative of composition (C₆H₅CH=NN=CHC₆H₅)Fe₂(CO)₆ to which the structure I was assigned. The N–N bond of

(1) (a) University of Waterloo. (b) McMaster University.

(2) H. W. Quinn and J. H. Tsai, *Advan. Inorg. Chem. Radiochem.*, **12**, 217 (1969).

(3) (a) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **6**, 20 (1967); (b) M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Commun.*, 543 (1965).

4,4'-dimethylbenzophenone azine is cleaved by Fe-(CO)$_5$[3b] to yield a bridged diiron hexacarbonyl derivative.[4] Reactions of pyridazine and 3,6-diarylpyridazines with iron carbonyls have recently been reported.[5] Several metal carbonyl complexes from 1,4- and 1,2-diazabutadienes have been synthesized.[6] In these compounds, the N–N bond is retained and the ligands behave as two (or four) electron donors *via* the nitrogen atoms. A number of studies pertaining to the reactions of nitrogen heterocycles containing N=N bonds, of which 2,3-diazabicyclo[2.2.1]heptene-2 and 1-pyrazolines are typical, with metal carbonyls have recently been reported.[7] Apart from the above reports and unsuccessful attempts to prepare methyleneamino derivatives of $[\pi$-C$_5$H$_5$M(CO)$_3]_2$ (M = Mo, W) from R^{1}R^{2}C= NN=CR^{1}R^2 (R^1 = R^2 = CH$_3$ or C$_6$H$_5$; R^1 = C$_6$H$_5$, R^2 = H),[8] the reactions of azines with transition metal organometallics have been neglected.

In sharp contrast, an increasing number of compounds which can be formally considered to contain azine fragments are known.[9] These include, among others, nitrogen-bridged iron carbonyl complexes derived from (C$_6$H$_5$)$_2$C=NNH[10a] and (C$_6$H$_5$)$_2$C=NN[10b] as well as a variety of π-cyclopentadienylmolybdenum and -tungsten compounds obtained from the reaction of $[\pi$-C$_5$H$_5$M(CO)$_3]_2$ (M = W, Mo) with diphenylmethyleneaminotrimethylsilane.[8,11] The ligand properties of (CF$_3$)$_2$C=N$^-$ have also been described.[12] Also related to this work are metal carbonyl complexes of the Schiff bases ArCR=NR' investigated by Pauson and coworkers[13] and the numerous reported reactions of azo compounds with organometallic reagents, which have recently attracted interest in view of the orthometalation reaction.[14,15]

The work described herein concerns the reactions of two heterocyclic azines, 3,5,7-triphenyl-4H-1,2-diazepine (II, Diaz) and 3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine (III, Diaz H$_2$) with Fe$_2$(CO)$_9$, Ru$_3$(CO)$_{12}$, and [Rh(CO)$_2$Cl]$_2$, These compounds were specifically chosen because of their similarity to 1,3,5-cycloheptatriene and 1,3-cycloheptadiene, both of which form a variety of π-bonded organometallic derivatives. We were particularly interested to know how the ligand properties of 1,3,5-cycloheptatriene are modified by introduction of two adjacent nitrogen atoms into the ring. The parent compound 4H-1,2-diazepine has not
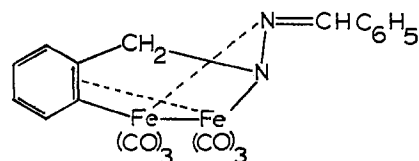
I
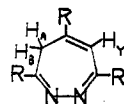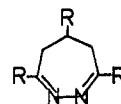
II (R=C$_6$H$_5$)   III (R=C$_6$H$_5$)

yet been synthesized. Preliminary reports of part of this work have appeared.[16,17]

Experimental Section

3,5,7-Triphenyl-4H-1,2-diazepine was synthesized by the methods of Buchardt and coworkers[18] and Kan, Snieckus, and Klingsberg.[19] 3,5,7-Triphenyl-4,5,6-trihydro-1,2-diazepine was prepared by the reaction of hydrazine hydrate with benzaldiacetophenone in ethylene glycol.[20]

All chromatographic separations were carried out on neutral alumina or silica gel under nitrogen using degassed solvents. Infrared spectra were measured on Beckman IR 10 and IR 9 spectrophotometers; nmr spectra were measured on Varian HA-100 and T-60 instruments. Chemical shifts were on the δ scale, downfield from internal TMS. Mass spectra were recorded on an Hitachi Perkin-Elmer RMU-6E spectrometer. Mössbauer data were accumulated as previously described.[21]

Reaction of Diaz with Fe$_2$(CO)$_9$.—The diazepine (1.28 g, 3.97 mmol) was stirred for 8 hr at room temperature in the dark under nitrogen with Fe$_2$(CO)$_9$ (2.5 g, 6.87 mmol) in benzene (150 ml). The red solution was evaporated to dryness and the solid extracted with cyclohexane (50 ml). The volume of this solution was reduced on a rotary evaporator and chromatographed on alumina. Elution with cyclohexane gave a deep red band as the first and major component. Recrystallization was from *n*-hexane. The red crystals had mp 137° (14.3%). *Anal.* Calcd for (C$_{23}$H$_{18}$N$_2$)Fe$_2$(CO)$_6$: C, 57.84; H, 3.01; N, 4.65; O, 15.93. Found: C, 57.75; H, 2.99; N, 4.50; O, 15.21.

A substantial amount of 2,4,6-triphenylpyridine (identified by comparison with an authentic sample) was obtained as an impurity when the initial red solid was recrystallized from benzene. Later experiments showed that the iron carbonyl complex decomposed on the alumina column to yield 2,4,6-triphenylpyridine.

Improved yields (40%) of the iron complex were found when the quaternary salt [C$_{23}$H$_{18}$N$_2$H]BF$_4$[22] was used as a starting material.

Reaction of Diaz H$_2$ with Fe$_2$(CO)$_9$.—The diazepine (0.64 g, 2.0 mmol) was stirred at room temperature in benzene with an excess of Fe$_2$(CO)$_9$ for 10 hr. Extraction with pentane followed by silica gel chromatography yielded, on elution with a 4:1 mixture of petroleum ether (bp 60–80°) and benzene, two bands. The initial yellow eluent was discarded in view of the minute quantity. The deep red band which followed was partially separated into two red components on slow elution. The two fractions had identical infrared spectra, and repeated chromatography failed to give a complete separation. Crystallization of the red fractions was then accomplished by standing at 0° under nitrogen for 2 weeks, mp 125–130° dec. *Anal.* Calcd

(4) D. Bright and O. S. Mills, *Chem. Commun.*, 245 (1967).

(5) (a) R. P. Bennett, *Inorg. Chem.*, **9**, 2184 (1970); (b) A. N. Nesmeyanov, L. V. Rybin, M. I. Rybinskaya, A. V. Arutyungan, N. T. Gubenko, and P. V. Petrovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **7**, 1574 (1971); *Chem. Abstr.*, **75**, 94183 (1971).

(6) H. T. Dieck, I. W. Renk, and H. P. Brehm, *Z. Anorg. Allg. Chem.*, **379**, 169 (1970).

(7) (a) M. Herberhold and W. Golla, *J. Organometal. Chem.*, **26**, C27 (1971), and references therein; (b) H. Kisch, *ibid.*, **30**, C25 (1971).

(8) K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc. A*, 2279 (1970).

(9) The literature on these compounds is extensive, and azine fragments have been obtained from a variety of organonitrogen compounds having N–N bonds. We make no attempt to be comprehensive here.

(10) (a) M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Commun.*, 1106 (1967); (b) P. E. Baikie and O. S. Mills, *ibid.*, 1228 (1967).

(11) H. R. Keable and M. Kilner, *ibid.*, 349 (1971).

(12) B. Cetinkaya, M. F. Lappert, and J. McMeeking, *ibid.*, 215 (1971).

(13) W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 2077 (1969).

(14) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(15) (a) A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Commun.*, 168 (1971), and references therein; (b) M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *ibid.*, 661 (1971).

(16) A. J. Carty, D. P. Madden, M. Mathew, G. J. Palenik, and T. Birchall, *ibid.*, 1664 (1970).

(17) R. A. Smith, D. P. Madden, A. J. Carty, and G. J. Palenik, *ibid.*, 427 (1971).

(18) O. Buchardt, C. L. Pedersen, U. Svanholm, A. M. Duffield, and A. T. Balaban, *Acta Chem. Scand.*, **23**, 3125 (1969).

(19) G. Kan, V. Snieckus, and E. Klingsberg, unpublished results.

(20) R. G. Amiet and R. B. Johns, *Aust. J. Chem.*, **21**, 1279 (1968).

(21) T. Birchall, *Can. J. Chem.*, **47**, 1351 (1969).

(22) G. Kan, D. P. Madden, V. Snieckus, and A. J. Carty, unpublished results.

for $(C_{23}H_{20}N_2)Fe_2(CO)_6$: C, 57.65; H, 3.34; N, 4.64. Found: C, 58.16; H, 3.53; N, 4.65.

Reaction of [Rh(CO)₂Cl]₂ with Diaz.—[Rh(CO)₂Cl]₂ (0.15 g) and Diaz (0.25 g) were stirred in benzene for 13 hr. The solution was taken to dryness, dissolved in CHCl₃, and filtered. Addition of *n*-heptane and cooling gave a yellow crystalline solid. Recrystallization several times from benzene–heptane gave the product, mp 144–147° dec. *Anal.* Calcd for $(C_{23}H_{18}N_2)Rh$-(CO)₂Cl: C, 58.10; H, 3.51; N, 5.42; mol wt, 516. Found: C, 58.50; H, 3.44; N, 5.33; mol wt (osmometric in C_6H_6), 510.

The above complex reacted in benzene with 2 mol of Ph₃P to give quantitative yields of 3,5,7-triphenyl-4*H*-1,2-diazepine and Rh(CO)Cl(Ph₃P)₂. The latter was identified by its characteristic infrared spectrum.

An analogous reaction to the above using [Rh(CO)₂Br]₂ (from the chloride (0.1 g) and KBr (0.15 g) in acetone) gave Rh(CO)₂Br-(Diaz) as lemon crystals. *Anal.* Calcd for $(C_{23}H_{18}N_2)Rh$-(CO)₂Br: C, 53.50; H, 3.23; N, 4.99; mol wt, 561. Found: C, 53.51; H, 3.43; N, 4.70; mol wt (osmometric in C_6H_6), 561.

Reaction of [Rh(CO)₂Cl]₂ with Diaz H₂.—[Rh(CO)₂Cl]₂ (0.1 g) and the diazepine (0.06 g) in benzene (100 ml) were stirred at room temperature for 3 hr. A few milliliters of *n*-heptane was added and the solution cooled. Orange crystals were obtained. *Anal.* Calcd for $(C_{23}H_{10}N_2)[Rh(CO)_2Cl]_2$: C, 45.47; H, 3.83; N, 3.93; mol wt, 713. Found: C, 46.21; H, 2.81; N, 4.02; mol wt (osmometric in C_6H_6), 724.

A similar reaction using [Rh(CO)₂Br]₂ gave orange crystals of [Rh(CO)₂Br]₂(Diaz H₂). *Anal.* Calcd for $(C_{23}H_{20}N_2)[Rh$-(CO)₂Br]₂: C, 40.43; H, 2.15. Found: C, 39.71; H, 2.66.

Reaction of Diaz with Ru₃(CO)₁₂.—A mixture of Ru₃(CO)₁₂ (0.5 g, 0.78 mmol) and Diaz (0.75 g, 2.32 mmol) in degassed benzene (120 ml) was stirred at 50° under nitrogen for 50 hr. The red solution was filtered and evaporated to dryness. The solid was extracted several times with cyclohexane, and the solutions were chromatographed on alumina. The first band eluted was unreacted Ru₃(CO)₁₂. Traces of red and violet compounds were then successively eluted, but the quantities of these products were too small for identification. The main yellow band which was eluted next afforded lemon yellow crystals on evaporation of the solvent. This product was recrystallized from benzene–cyclohexane, mp 235–236°. *Anal.* Calcd for $(C_{23}H_{18}N_2)_2Ru(CO)_3$: C, 70.91; H, 4.37; N, 6.75. Found: C, 70.82; H, 4.05; N, 6.67.

Reaction of Diaz H₂ with Ru₃(CO)₁₂.—Ru₃(CO)₁₂ (0.4 g) and the diazepine (0.41 g) were refluxed in benzene (100 ml) for 60 hr. The solvent was removed *in vacuo*. Preliminary attempts at separation of the products using tlc indicated the presence of four compounds. The reaction residue was extracted with *n*-hexane (50 ml) and the solution chromatographed on silica gel. Slow elution using 50:50 petroleum ether–benzene gave a minute amount of a yellow compound. Continued elution gave a second yellow compound also in small yield. This material was recrystallized from *n*-heptane at −78°. The product was identified as Ru₃(CO)₉(Diaz H₂) by analysis and single-crystal X-ray measurements. *Anal.* Calcd for $(C_{23}H_{20}N_2)Ru_3(CO)_9$: C, 43.65; H, 2.46; N, 3.18. Found: C, 44.51; H, 2.84; N, 3.29. X-Ray measurements[23] showed the following: Ru₃(CO)₉-$(C_{23}H_{20}N_2)$, triclinic crystals; space group $P\bar{1}$; $a = 14.04$ Å, $b = 10.40$ Å, $c = 10.95$ Å; $\alpha = 103° 6'$, $\beta = 98° 50'$, $\gamma = 90° 15'$, $U = 1536$ Å³; $\rho_{measd} = 1.816$ g cm⁻³, ρ_{calcd} (for $Z = 2$, $M = 879.7$) $= 1.902$ g cm⁻³.

Results and Discussion

Iron Complexes. (1) $(C_{23}H_{18}N_2)Fe_2(CO)_6$.—Previous studies of reactions between iron carbonyls and functionalized 1(1*H*),2-diazepines including 1-methyl-3,5,7-triphenyl-1(1*H*),2-diazepine have yielded (diene)Fe(CO)₃ complexes.[24] With Fe₂(CO)₉, Diaz yields only (Diaz)Fe₂(CO)₆ and 2,4,6-triphenylpyridine.

The infrared spectrum of Fe₂(CO)₆(Diaz) (Table I) shows five CO stretching bands in *n*-hexane, with a shoulder on the lowest band. This spectrum can be compared with that of $(C_{12}H_8N_2)Fe_2(CO)_6$[5] (CS₂;

(23) We thank Dr. M. W. Bartlett for these measurements.

(24) A. J. Carty, G. Kan, D. P. Madden, V. Snieckus, M. Stanton, and T. Birchall, *J. Organometal. Chem.*, **32**, 241 (1971).

TABLE I
INFRARED SPECTRA OF DIAZEPINE COMPLEXES

| Compound	ν(C–O), cm⁻¹
$(C_{23}H_{18}N_2)Fe_2(CO)_6$	2068 m, 2031 vs, 1998 vs, 1986 s, 1972 sh, 1967 m (C_6H_{14}); 2058 s, 2016 vs, 1980 vs, 1963 s, 1942 vs (mull)
$(C_{23}H_{20}N_2)Fe_2(CO)_6$	2067 m, 2060 m, 2029 s, 2020 m, 1993 s, 1988 m, 1978 m, 1964 m (C_6H_{14}); 2056 s, 2002 vs, br, 1977 s, 1966 s, 1951 s, 1913 s (mull)
$(C_{23}H_{18}N_2)Rh(CO)_2Cl$	2086 vs, 2014 vs (CHCl₃); 2078 s, 2010 s (mull)
$(C_{23}H_{18}N_2)Rh(CO)_2Br$	2079 vs, 2008 vs (C_6H_6); 2078 s, 2005 s (mull)
$(C_{23}H_{20}N_2)[Rh(CO)_2Cl]_2$	2092 vs, 2081 s, 2027 vs, 2010 sh (C_6H_6); 2090 s, 2079 s, 2029 s, 2017 s (mull)
$(C_{23}H_{20}N_2)[Rh(CO)_2Br]_2$	2091 s, 2081 s, 2027 s, 2010 sh (C_6H_6); 2088 s, 2078 s, 2030 s, 2016 s (mull)
$(C_{23}H_{20}N_2)Ru_3(CO)_9$	2090 vs, 2056 vs, 2045 vs, 2032 m, 2016 vs, 2011 sh, 1996 m, 1983 s, 1974 m, 1963 w (C_6H_{14})
$(C_{46}H_{36}N_4)Ru(CO)_3$	2017 s, 1950 s, br (CH₂Cl₂); 2000 s, 1935 s (mull)
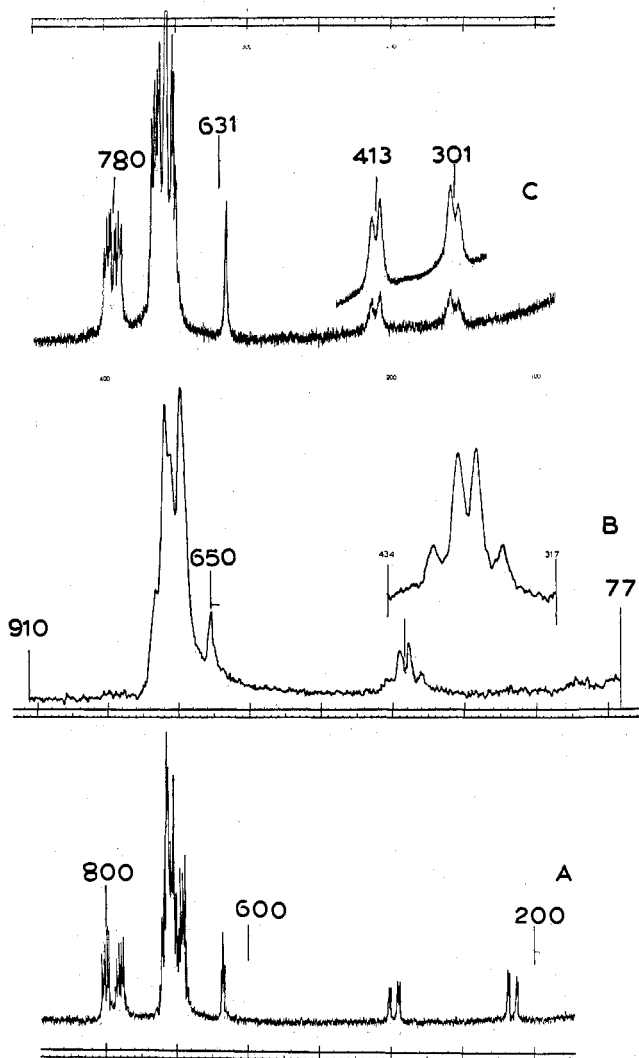
Figure 1.—The 100-MHz nmr spectra in C_6D_6 of (A) $C_{23}H_{18}N_2$, (B) $(C_{23}H_{18}N_2)Fe_2(CO)_6$, and (C) $(C_{23}H_{18}N_2)Rh(CO)_2Cl$. Line positions given are in Hz downfield from tetramethylsilane at 0.00 Hz.

2073, 2033, 1989, 1972 cm^{-1}) which has a symmetrical nitrogen-bridged structure and to (C$_4$H$_8$N$_2$)Fe$_2$(CO)$_6$ (Nujol; 2064 (vs), 2020 (vs), 1990 (vs), 1974 (vs), 1964 (vs), 1935 (w) cm^{-1})[25] with an unsymmetrical bridged structure. In the region 1650–700 cm^{-1} the ligand infrared spectrum shows none of the frequency shifts usually encountered on coordination of ring >C=C< or >C=N-.[2,24] The 100-MHz nmr spectrum of Fe$_2$(CO)$_6$(Diaz) in benzene-d_6 together with the free ligand spectrum is given in Table II. Figure 1 illustrates the

TABLE II
NMR SPECTRA OF DIAZEPINES AND COMPLEXES (δ SCALE)

Compound	
II	6.39 t (vinyl H); 4.04 d, 3.91 d (exo H$_A$) J_{AX} = 2.4 Hz; 2.37 d, 2.25 d (endo H$_B$) J_{BX} = 1.6 Hz; J_{AB} = 12.1 Hz; 7.04 m (phenyl H); 7.80 m (phenyl H); 8.00 m (phenyl H)
III	2.65 d (CH$_2$, $J_{H_5-CH_2}$ = 7.2 Hz); 3.55 quintet (H$_5$); 6.75–7.16 m (phenyl H; 7.76 m (phenyl H)
(C$_{23}$H$_{18}$N$_2$)Fe$_2$(CO)$_6$	4.02 s, 3.85 s, 3.72 s, 3.55 s (AB quartet, CH$_2$; J_{AB} = 17.0 Hz), 6.50 s (vinyl H); 7.06 m (phenyl H)
(C$_{23}$H$_{18}$N$_2$)Rh(CO)$_2$Cl	4.13 d, 3.01 d (AB quartet, CH$_2$, J_{AB} = 11.7 Hz); 6.20 s (vinyl H); 7.03 m (phenyl H); 7.80 m (phenyl H)
(C$_{23}$H$_{20}$N$_2$)[Rh(CO)$_2$Cl]$_2$	3.45 d (CH$_2$, $J_{H_5-CH_2}$ = 5.0 Hz); 4.05 quintet (H$_5$); 7.08 m, 7.63 m, 8.16 m (phenyl H)

the methylene protons H$_A$ and H$_B$ are much nearer to nmr equivalence than in the free diazepine, the CH$_2$ spectrum of the latter having more "AX" character. J_{AB} is increased from 12.1 ppm in II to 17 ppm in Fe$_2$(CO)$_6$(Diaz) while the chemical shift difference in the AB spectrum decreases to 25 ppm from 166 ppm. These results indicate that while the ring substituents are the same in Fe$_2$(CO)$_6$(Diaz) and II, a major conformational change in the ring system has occurred on complexation. Moreover, substantial shielding of ortho protons on the benzene rings attached to positions 3 and 7 of II occurs on complexation presumably as a result of the proximity of these protons to the Fe$_2$(CO)$_6$ fragment. Further analysis of the nmr spectrum, in the light of the X-ray structure of this compound, is presented later.

The mass spectrum (Table III) does not exhibit a parent ion peak but shows consecutive loss of five CO groups affording the ion [Fe$_2$(Diaz)]$^+$ in 14% abundance. Fragmentation of this ion proceeds partially by loss of C$_6$H$_5$CN, a common fragmentation pathway for 2-phenyl-substituted nitrogen heterocycles.[18,26] The base peak in the spectrum is, however, the 2,4,6-triphenylpyridine molecule ion. Although the production of triphenylpyridine by thermal decomposition of the complex in the mass spectrometer cannot be completely ruled out, mass spectra were obtained with inlet temperatures well below the melting point of the complex. The ion of m/e 307 may therefore arise *via* loss of the fragment Fe$_2$NH rather than from successive elimination of

TABLE III
MASS SPECTRA OF (C$_{23}$H$_{18}$N$_2$)Fe$_2$(CO)$_6$, (C$_{23}$H$_{20}$N$_2$)Fe$_2$(CO)$_6$, AND C$_{23}$H$_{20}$N$_2$

	(C$_{23}$H$_{18}$N$_2$)Fe(CO)$_6$			(C$_{23}$H$_{20}$N$_2$)Fe$_2$(CO)$_6$			C$_{23}$H$_{20}$N$_2$	
m/e	Abundance	Ion	m/e	Abundance	Ion	m/e	Abundance	Ion
574	8[a]	(P − CO)$^+$	576	1	(P − CO)$^+$	325	25	(P + H)$^+$
546	15[a]	(P − 2CO)$^+$	548	1	(P − 2CO)$^+$	324	100	P$^+$
518	9[a]	(P − 3CO)$^+$	520	1	(P − 3CO)$^+$	323	7	
490	3[a]	(P − 4CO)$^+$	492	1	(P − 4CO)$^+$	296	8	(P − N$_2$)$^+$
462	17[a]	(P − 5CO)$^+$	464	2	(P − 5CO)$^+$	247	7	(P − C$_6$H$_5$)$^+$
434	14	(P − 6CO)$^+$ ≡ Fe$_2$L$^+$	436	5	(P − 6CO)$^+$ ≡ Fe$_2$L$^+$	221	5	(P − C$_6$H$_5$CN)$^+$
331	10	(Fe$_2$L$^+$ − C$_6$H$_5$CN)$^+$	324	10	L$^+$	220	10	(P − C$_6$H$_5$C$_2$H$_3$)$^+$
307	100	(C$_{23}$H$_{17}$N)$^+$	311	5		218	8	
230	55	(C$_{17}$H$_{12}$N)$^+$	307	5	(C$_{23}$H$_{17}$N)$^+$	206	9	(P − C$_6$H$_5$C$_3$H$_5$)$^+$
219	84	(Fe$_2$L$^+$ − Fe$_2$ − C$_6$H$_5$CN)$^+$	219	5		205	18	((C$_6$H$_5$)$_2$C$_4$H$_3$)$^+$
202	40	(C$_{16}$H$_{15}$)$^+$	207	7		193	6	((C$_6$H$_5$)$_2$C$_3$H$_3$)$^+$
191	39	(C$_{15}$H$_{11}$)$^+$	197	60	(C$_6$H$_5$C$_3$N$_2$Fe)$^+$	192	7	((C$_6$H$_5$)$_2$C$_3$H$_2$)$^+$
189	28		168	100	(C$_2$H$_4$N$_2$Fe$_2$)$^+$	191	10	((C$_6$H$_5$)$_2$C$_3$H)$^+$
127	12		140	24	Fe$_2$N$_2$$^+$	189	5	
115	45		130	7		130	58	((C$_6$H$_5$)C$_2$N$_2$H)$^+$
103	95	(C$_6$H$_5$CN)$^+$	112	57	Fe$_2$$^+$	117	7	((C$_6$H$_5$)C$_3$H$_4$)$^+$
102	40	(C$_6$H$_4$CN)$^+$	104	16		116	41	((C$_6$H$_5$)C$_2$NH)$^+$
89	25	(C$_6$H$_5$C)$^+$	103	13	(C$_6$H$_5$CN)$^+$	114	12	
77	52	(C$_6$H$_5$)$^+$	84	(270)[b]	FeN$_2$$^+$	104	13	
76	75	(C$_6$H$_4$)$^+$	82	15		103	20	(C$_6$H$_5$CN)$^+$
63	36	(C$_4$H$_5$N)$^+$	77	13	(C$_6$H$_5$)$^+$	91	12	
56	20	Fe$^+$	68	24	(C$_4$H$_6$N)$^+$	77	43	(C$_6$H$_5$)$^+$
51	50		56	100	Fe$^+$	51	9	
50	55							

[a] Abundances of these ions are expressed relative to m/e 434 ion = 100. [b] Abundances are expressed relative to m/e 168 ion = 100. On this basis m/e 84 = 270.

changes which accompany coordination of the diazepine to the Fe$_2$(CO)$_6$ and Rh(CO)$_2$Cl moieties in Fe$_2$(CO)$_6$(Diaz) and [Rh(CO)$_2$Cl](Diaz), respectively. A downfield shift of the vinyl and methylene resonances in II occurs on formation of the iron complex. Furthermore

NH, Fe, and Fe from [(C$_{23}$H$_{18}$N$_2$)Fe$_2$]$^+$ since no evidence was found for (C$_{23}$H$_{18}$N$_2$)$^+$, (C$_{23}$H$_{18}$N$_2$Fe)$^+$, or (C$_{23}$H$_{17}$NFe$_2$)$^+$. In this connection it is worth noting that 1-substituted-3,5,7-triphenyl-1(1H),2-diazepines decompose both thermally and by electron impact, *via*

(25) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **8**, 2514 (1969).

(26) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 566–644.

loss of nitrene species.[27] Likewise, in the mass spectrum of (1-methyl-3,5,7-triphenyl-1(1H),2-diazepine)-tricarbonyliron(0), the ion $(C_{24}H_{20}N_2Fe)^+$ fragments by loss of methylnitrene to give $(C_{23}H_{17}NFe)^+$.[24] Loss of Fe from this ion again gives the triphenylpyridine molecule ion in high abundance. The mass spectrum, in contrast to that of II,[18] provides no evidence for a direct N–N bond.

The ^{57}Fe Mössbauer spectrum of $Fe_2(CO)_6(Diaz)$ consists of three lines. A least-squares computer fit to Lorentzian line shapes indicates approximate area ratios of 2:1:1. The spectrum clearly indicates the presence of two iron sites, a feature which was readily explicable only after completion of the X-ray study. For a three-line spectrum only two assignments are possible. Naming the nonequivalent iron atoms Fe(1) and Fe(2) and numbering the lines 1–3 from left to right these assignments are shown in Table IV. Assignment

TABLE IV

		δ, mm sec^{-1}	ΔE_Q, mm sec^{-1}
1(a)	Line 1	−0.25	0
	Lines 2 and 3	+0.82	0.26
1(b)	Lines 1 and 2	+0.22	0.93
	Lines 1 and 3	+0.35	1.19

a can be eliminated in view of the negative isomer shift for line 1 as well as the zero quadrupole splitting and hence near cubic environment for the iron site giving rise to this unsplit resonance. Assignment b gives Fe(1) and Fe(2) similar isomer shifts, a fact consistent with the molecular geometry (*vide infra*).

Our initial analytical and spectroscopic measurements, while suggesting an $Fe_2(CO)_6$ derivative similar to di-μ-(4,4′-dimethylbenzophenoniminato)-bis(tricarbonyliron),[4] did not explain the presence of two nonequivalent iron atoms observed in the Mössbauer spectrum[28] or indicate the geometry of the diazepine ring. An X-ray structural study of $Fe_2(CO)_6(Diaz)$[16] revealed the stereochemistry shown in Figure 2.[29] As expected from the mass spectral data the N–N bond of the diazepine has been cleaved. Two Fe(CO)$_3$ units have been inserted into the N–N bond[30] with each N atom bridging two iron atoms. The nitrogen atoms behave as three electron donors. The complex is thus μ-(1,3,5-triphenyl-2-pentene-1,5-diiminato)-bis(tricarbonyliron) and the two iron atoms form part of a bicyclo[5.1.1] system.

A number of complexes with similar nitrogen bridges are now known.[31] The stereochemistry of such systems bears a striking resemblance to analogous sulfur- and phosphorus-bridged species.[31] Consideration of the molecular structure immediately reveals the source of Mössbauer nonequivalence of Fe(1) and Fe(2). The Fe(1)–N (1.920 Å average) and Fe(2)–N (1.965 Å average) bond lengths are significantly different. A long Fe(2)–C(6) bond (1.804 Å) is presumably a consequence of the proximity of phenyl groups on C(7)
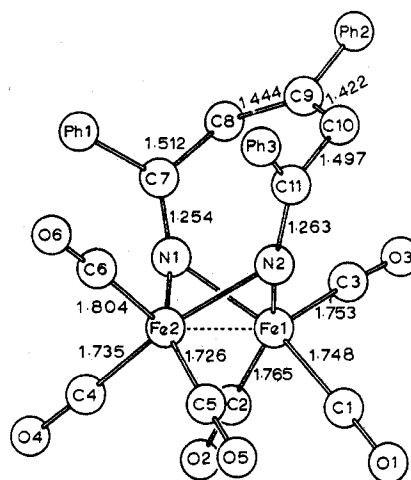
(27) V. Snieckus and G. Kan, *Chem. Commun.*, 1208 (1970).

(28) The crystal structure analysis of di-μ-(4,4′-dimethylbenzophenoniminato)-bis(tricarbonyliron) shows two equivalent iron atoms.[4]

(29) Complete details of the structure will be presented elsewhere.

(30) The N–N distance of 2.248 (7) Å is much longer than that expected for an N–N single bond.

(31) For a summary see ref 2–7, 13–15, and R. J. Doedens, *Inorg. Chem.*, **9**, 429 (1970).

Figure 2.—The molecular structure of $(C_{23}H_{18}N_2)Fe_2(CO)_6$. The Fe(1)–Fe(2) distance of 2.39 Å, Fe(1)–N(1) of 1.92 Å, Fe(1)–N(2) of 1.010 Å, Fe(2)–N(1) of 1.960 Å, and Fe(2)–N(2) of 1.969 Å are not shown.

and C(11) to the carbonyl group C(6)–O(6). The net result of the asymmetry of the coordinated diazepine appears to be rather weaker bonding between the bridging nitrogen atoms and Fe(2), together with a larger distortion from octahedral symmetry at Fe(2). In this light, we predict a lower s electron density at the nucleus of Fe(2) and a somewhat larger deviation from cubic symmetry. Hence we assign an isomer shift of 0.35 mm sec^{-1} and quadrupole splitting of 1.19 mm sec^{-1} to Fe(2) (Table V).

TABLE V
MÖSSBAUER PARAMETERS FOR IRON COMPLEXES[a]

Compound	δ, mm sec^{-1}	ΔE_Q, mm sec^{-1}	T, °K
$(C_{23}H_{18}N_2)Fe_2(CO)_6$	0.22	0.93 Fe(1)	78
	0.35	1.19 Fe(2)	
$(C_{23}H_{20}N_2)Fe_2(CO)_6$	0.19	0.77 Fe(1)	78
	0.31	1.49 Fe(2)	

[a] Relative to sodium nitroprusside.

From the Mössbauer data Fe(1) has a greater share in the electron density originating from the two nitrogen atoms. A contribution from resonance form IV would
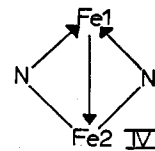
be expected to leave Fe(2) electron deficient, as is observed. When represented in this way, the immediate electronic environment of Fe(2) resembles that of one iron atom in the complex (ffos)Fe$_2$(CO)$_6$,[32] for which the Mössbauer parameters $\delta = 0.32$, $\Delta E_Q = 1.30$ mm sec^{-1} have been obtained.

The conformation of the N_2C_5 diazepine moiety differs considerably from that found in [Rh(CO)$_2$Cl](Diaz) (compare Figures 2 and 4). The five carbon atom fragment of the ligand deviates less from planarity than in the rhodium complex, with the ligand residue being folded about the C(7)–C(11) axis (Figure 2). The

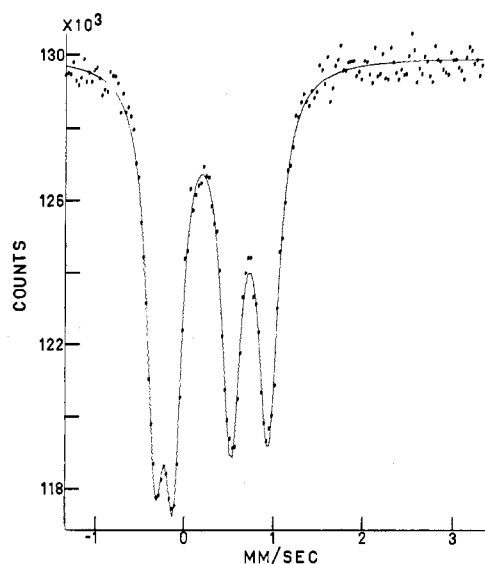(32) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *ibid.*, **8**, 95 (1969).

Figure 3.—The ^{57}Fe Mössbauer spectrum of $(C_{23}H_{20}N_2)Fe_2(CO)_6$ at 78°K.

overall effect is to make H_A and H_B of II stereochemically nearer equivalence in $Fe_2(CO)_6(Diaz)$ than in $[Rh(CO)_2Cl](Diaz)$ or the free ligand. This is clearly shown by the nmr spectra (Figure 1).

It is of interest that II does not yield a π-bonded azadiene complex on reaction with $Fe_2(CO)_9$. Presumably the poor coordinating ability of a $>C=N-$ bond together with the weakness of the N—N bond in II contributes to the reaction sequence. Although a number of organic nitrogen compounds containing N—N bonds have now been reacted with iron carbonyls,[31] it is not clear at the present time which electronic and structural factors affect N—N and N=N bond reactivities. Thus the N—N bond of 4,4'-dimethylbenzophenone azine is cleaved by iron carbonyls[3,4] whereas the N—N bond of benzaldehyde azine remains intact under similar conditions.[2] Similarly the N=N double bond of $CH_3N=NCH_3$ is reduced to a single bond on formation of an $Fe_2(CO)_6$ complex[32,33] while $C_6H_5N=NC_6H_5$ is completely rearranged to the *o*-semidine skeleton by $Fe_2(CO)_9$.[13] We are currently investigating the effect of the groups R in $R_2C=NN=CR_2$ on the reactivity of the N—N bond toward metal carbonyls.

(2) $(C_{23}H_{20}N_2)Fe_2(CO)_6$.—The reaction of the diazepine III with $Fe_2(CO)_9$ proceeds in similar fashion to II, giving a red–brown $Fe_2(CO)_6$ complex having an infrared spectrum under low resolution which is virtually identical with that of $Fe_2(CO)_6(Diaz)$. Under high resolution conditions the three highest frequency bands appear as doublets. In the mass spectrum peaks corresponding to $[Fe_2(CO)_{5-n}(C_{23}H_{20}N_2)]$ ($n = 1–5$) were evident. The base ion was at m/e 84 (FeN_2^+). Ions of major abundance in the complex appeared below m/e 200. Although the fragmentation pattern was not obvious due to the lack of ions in high abundance between m/e 436 $(Fe_2L)^+$ and m/e 140, the appearance of the ions $(C_6H_5N_2Fe_2)^+$ $(m/e$ 168) and Fe_2^+ $(m/e$ 112) confirmed the binuclear nature of the complex and coordination of the two nitrogen atoms of the heterocycle.

The Mössbauer spectrum of 2 is shown in Figure 3.

(33) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

The solid curve represents a least-squares computer fit to Lorentzian line shapes. The spectrum is similar to that of $Fe_2(CO)_6(Diaz)$ except that the line at lowest velocity is resolved into a doublet. The three possible assignments are listed in Table VI. Assignment 1 can be

TABLE VI

		δ, mm sec^{-1}	ΔE_Q, mm sec^{-1}
2(a)	Lines 1 and 2	−0.37	0.24
	Lines 3 and 4	+0.82	0.48
2(b)	Lines 1 and 3	+0.07	1.01
	Lines 2 and 4	+0.43	1.25
2(c)	Lines 2 and 3	+0.19	0.77
	Lines 1 and 4	+0.31	1.49

ruled out as previously mentioned. From a comparison with the Mössbauer parameters for $Fe_2(CO)_6(Diaz)$, we prefer assignment 2(c). This is still consistent with similar δ values for Fe(1) and Fe(2) and an analogous structure but with a greater distortion from octahedral symmetry at Fe(2). This is expected in view of the increased asymmetry arising from the more puckered ring system of III. Mössbauer parameters extracted from the data are listed in Table III.

Rhodium Complexes. $[Rh(CO)_2X](Diaz)$ (X = Cl, Br).—With 3,5,7-triphenyl-$4H$-1,2-diazepine, $[Rh(CO)_2Cl]_2$ yields a complex analyzing as $[Rh(CO)_2Cl](Diaz)$. The analogous bromide was prepared by metathesis with potassium bromide. Both compounds are monomeric and exhibit two $\nu(CO)$ bands in the infrared typical of cis CO groups.[34] A single strong band at 313 cm^{-1} in $[Rh(CO)_2Cl](Diaz)$ disappears in the bromo analog and is assignable to $\nu(Rh–Cl)$ of an Rh–Cl bond trans to CO.[35] Although rather similar infrared spectral characteristics are exhibited by (olefin)Rh-$(CO)_2Cl$ compounds,[36] the ligand spectrum (1650–1400 cm^{-1}) does not change appreciably on coordination contrary to what might be expected for a complex having the $C=C$ bond of the diazepine coordinated to Rh(1). The appearance of a strong band at 725 cm^{-1} might characterize ortho-metalation on a benzene ring.[37] However, coordination of a nitrogen atom has also been found to effect substantial spectral changes in the C–H out-of-plane deformation region.[38] The nmr spectrum of $[Rh(CO)_2Cl](Diaz)$ (Table II) confirms the presence of the diazepine ring system, the nmr parameters being similar to II and different from $Fe_2(CO)_6(Diaz)$. The absence of a substantial chemical shift difference for the vinyl proton appears to rule out olefinic coordination to rhodium. Final details of the structure of the complex were resolved by an X-ray study.[17] Figure 4 shows the main structural features of interest. As expected the Rh atom is in the center of a square-planar arrangement consisting of two cis carbonyl groups, a chlorine atom trans to one carbonyl, and the diazepine ring, coordinated *via* a nitrogen atom, occupying the fourth position. The heterocycle is best described as a twisted boat form of the original diazepine, the molecule as a whole being folded about the N_1–C_4 axis and having a

(34) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

(35) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(36) J. Altman and G. Wilkinson, *J. Chem. Soc.*, 5654 (1964).

(37) A. Kasahara, *Bull. Chem. Soc. Jap.*, **41**, 1272 (1968).

(38) J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. S. Wilson, *Spectrochim. Acta, Part A*, **23**, 1121 (1967).
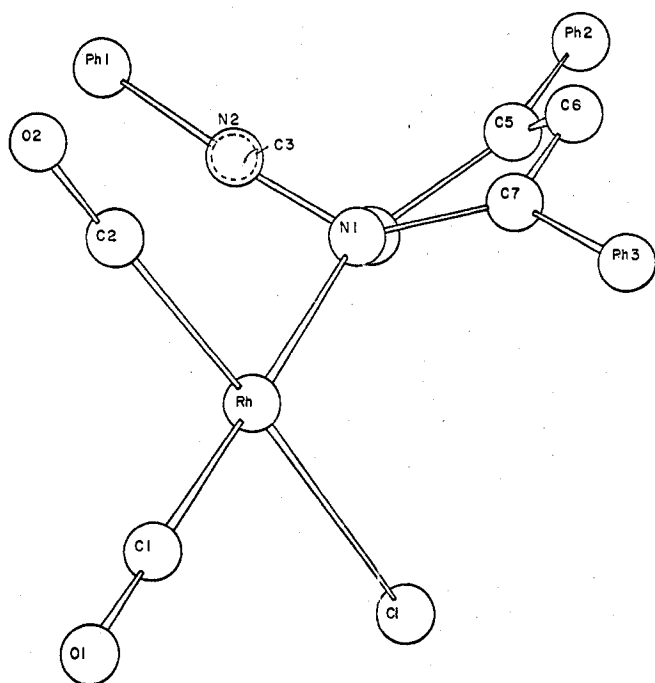
Figure 4.—The molecular structure of $(C_{23}H_{18}N_2)Rh(CO),Cl$ as viewed down the N(2)-C(3) axis.

fold of small magnitude along C_5–C_7 (Figure 4). The structure and conformation of the ring are of interest in view of the ambiguities which have recently been shown to exist in structural assignments made for seven-membered heterocycles based on spectroscopic measurements.[39] An X-ray structural determination[39] of the isomerized adduct from triphenylcyclopropene and diphenyl-*s*-tetrazine has revealed a 3,7-bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine structure rather than either of the two alternative structures previously proposed.[40] The above compound also exists in a twist-boat conformation in the solid state.

Comparison of nmr parameters for II and [Rh-(CO)$_2$Cl](Diaz) shows a somewhat smaller (110 ppm) chemical shift difference between the H_A and H_B in the complex and an absence of coupling between the vinyl proton H_Y and H_A and H_B but otherwise little change. In contrast to $Fe_2(CO)_6$(Diaz), the ortho protons on the phenyl substituents attached to the 3 and 7 positions of II are virtually unaffected by complexation to rhodium since the stereochemistry of the complex precludes a close approach of the ortho protons to the Rh(CO)$_2$Cl moiety.

These results elicit two conclusions. (a) The conformation of the free diazepine in solution is identical with that of the complexed heterocycle. If the complex is assumed to be undissociated in solution, in accord with molecular weight measurements, then the structure of the free ligand in solution is exactly that deduced from nmr measurements.[18] (b) Assuming (a) above, the complexed ligand must be undergoing a similar boat–chair interconversion in solution to that occurring in the free diazepine at room temperature. Since this inversion is readily amenable to study by nmr, the

rhodium complex offers a unique opportunity to study the effect of coordination on the thermodynamics of a boat–chair interconversion.

Finally, it is clear that reaction of [Rh(CO)$_2$Cl]$_2$ with II does not lead to N–N bond cleavage; the products are analogous to other square-planar Rh(1) complexes of the type Rh(CO)$_2$Cl·L (L = ammonia, pyridine, hydroxylamine, methyl cyanide)[41] for which, however, structural evidence was lacking. Interestingly, reactions of azoarenes with [Rh(CO)$_2$Cl]$_2$ yield complexes of type V which can be readily converted into monomeric acetates VI (M = Rh, X = CH$_3$COO) by treatment with sodium acetate.[15] With phenyl-substituted 1,2-diazepines we have as yet found no evidence for ortho-metalation reactions with rhodium compounds.

(3) **[Rh(CO$_2$)X]$_2$(Diaz H$_2$)** (X = Cl, Br).—Infrared and far-infrared (ν(Rh–Cl) 315 cm^{-1}) measurements on these compounds are indicative of square-planar Rh(1) with a similar disposition of ligands around each Rh as in [Rh(CO$_2$Cl)(Diaz)]. Molecular weight measurements conclusively demonstrate the dimeric nature of the chloro complex. Far-infrared spectra suggest the absence of bridging halide,[42] thus ruling out a structure based on a single bridging halogen. Nmr parameters for the chloro complex indicate retention of the ligand skeleton. The probable structure of the chloro complex is VII in which the diazepine functions as a bidentate bimetallic ligand. Molecular models indicate that with a slight rotation of one Rh(CO)$_2$X unit about the Rh–N bond such a structure is sterically feasible. Nitrogen-bridged [Rh(CO)$_2$Cl]$_2$L (L = 2,2'-bipyridyl) complexes have been reported by Lawson and Wilkinson.[34] The alternative, bridging *via* one nitrogen and one C=N, seems less probable.

Ruthenium Complexes.—The main product from Ru$_3$(CO)$_{12}$ and II is a yellow, air-stable crystalline complex, analyzing as Ru(CO)$_3$(C$_{23}$H$_{18}$N$_2$)$_2$. Only two ν(CO) bands one of which is broad are observed in the infrared spectrum. The 1600–700-cm^{-1} region resembles that of the complex [Rh(CO)$_2$Cl](Diaz) with no evidence for a drastic change in ligand structure. The appearance of a strong band at 750 cm^{-1} may indicate ortho disubstitution on a benzene ring. Attempts to obtain mass spectra failed owing to lack of volatility. A molecular weight measurement in chloroform, of limited accuracy owing to low solubility, yielded a value of 702, suggesting a monomeric formulation. The compound is quite stable, there being no reaction with PhEt$_2$P after stirring in benzene for 12 hr. The stability is difficult to reconcile with a simple disubstituted Ru(CO)$_5$ derivative. Indeed Ru(CO)$_3$L$_2$ complexes (L = nitrogen donor) have not apparently been synthesized. An alternative to a *cis*-Ru(CO)$_3$L$_2$ (L = Diaz H$_2$) structure, not inconsistent with the infrared and analytical data, is a structure of type VIII (M = Ru, X = CO) having two ortho-metalated benzene rings. Compounds of this type, several of which have been synthesized recently,[15] are known to be stable.
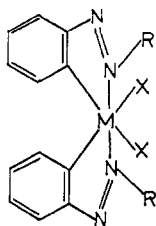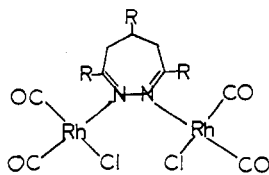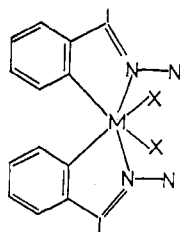
The complex (C$_{23}$H$_{20}$N$_2$)Ru$_3$(CO)$_9$ whose stoichiometry has been confirmed by X-ray analysis was the only product isolated from the reaction of III with Ru$_3$-

(39) J. N. Brown, R. L. Towns, and L. M. Trefonas, *J. Amer. Chem. Soc.*, **92**, 7436 (1970).

(40) (a) J. Sauer and G. Heinrichs, *Tetrahedron Lett.*, 4979 (1966); (b) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967).

(41) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, Chapter 6.
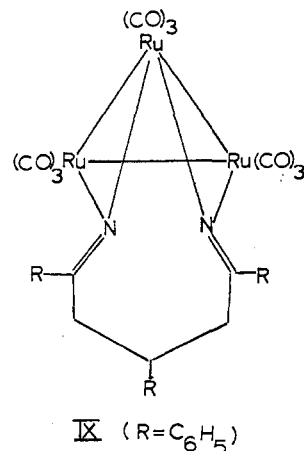
(42) No halogen-sensitive absorptions were observed below 300 cm^{-1} for [Rh(CO)$_2$Cl]$_2$(Diaz H$_2$).
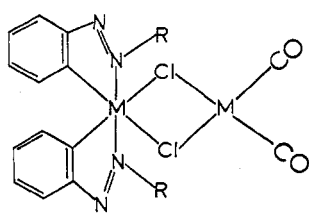
V $(R = C_6H_5)$ VI $(R = C_6H_5)$

VII $(R = C_6H_5)$ VIII

with $Fe_3(CO)_{12}$.[13] A suggested structure analogous to that proposed by Pauson and coworkers[13] is shown as IX.

IX $(R = C_6H_5)$

$(CO)_{12}$ in sufficient quantity for characterization. Infrared data (Table I) show nine $\nu(CO)$ bands and a ligand spectrum similar to that of the complex $Fe_2(CO)_6$-(Diaz). Complexes of similar composition have been reported as products from the reactions of azobenzenes

---

Formal Potentials and Cyclic Voltammetry of Some Ruthenium–Ammine Complexes

By HONG SUP LIM, DONALD J. BARCLAY, and FRED C. ANSON*

A number of formal redox potentials for $Ru^{III}(NH_3)_5L + e = Ru^{II}(NH_3)_5L$ and $Ru^{III}(NH_3)_4L_2 + e = Ru^{II}(NH_3)_4L_2$ (where L represents a variety of ligands) have been measured by cyclic voltammetry, potentiometry, and polarography. The trends in the potentials are discussed in terms of ligand properties, such as π-accepting capability. For three complexes, $Ru(NH_3)_5Pz^{2+}$ and *cis*- and *trans*-$Ru(NH_3)_4Pz_2^{2+}$, where $Pz \equiv$ pyrazine, the reduction of the coordinated ligand has been observed.

The solution chemistry of ruthenium–ammine complexes has received considerable attention[1] from a number of workers in recent years. The electrochemistry of these complexes, however, has been studied much less extensively. We report here on a number of aspects of the electrochemical behavior of some of the ruthenium–ammine complexes that we have been studying. One objective of the work was to compare the electrochemical behavior of reducible ligands coordinated to ruthenium(II) with their reduction when uncoordinated, in order to assess the extent to which metal-to-ligand back-bonding, a prominent feature in the coordination chemistry of ruthenium(II), influences the electrochemical reactivity of the ligands. Similar investigations, concentrating on the nitrosyl ligand, have been actively pursued by Mašek and coworkers.[2]

Experimental Section

Reagents.—$[Ru(NH_3)_5Cl]Cl_2$ was prepared as described in the literature either from $[Ru(NH_3)_6]Cl_3$[3] (Matthey Bishop Inc.) or from $RuCl_3$[4] (Research Organic/Inorganic Chemical Corp.). $[Ru(NH_3)_5Br]Br_2$ was prepared similarly by treating $Ru(NH_3)_6$-Cl_3 with refluxing HBr. *cis*- and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ were prepared as described by Gleu and Breuel.[5]

$[Ru(NH_3)_5NCS](ClO_4)_2$ was prepared as follows. A 2 m*M* solution of $Ru(NH_3)_5Cl^{2+}$ in 0.1 *M* $NaPF_6$ was reduced at a mercury pool electrode (−700 mV *vs.* sce) to yield $Ru(NH_3)_5H_2O^{2+}$. Excess sodium thiocyanate was added and the resulting orange-red solution was reoxidized at the electrode (−80 mV *vs.* sce) to give a wine red solution from which solid $[Ru(NH_3)_5NCS](ClO_4)_2$ was precipitated by addition of 5 *F* $NaClO_4$. The $Ru(NH_3)_5$-NCS^{2+} ion had absorption maxima at 495 nm (ϵ 3500) and 327 nm (ϵ 520).

(1) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(2) J. Mašek, *Inorg. Chim. Acta*, **3**, 99 (1969).

(3) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

(4) E. L. Farquhar, L. Rusnock, and S. J. Gill, *J. Amer. Chem. Soc.*, **92**, 416 (1970).

(5) K. Gleu and W. Breuel, *Z. Anorg. Allg. Chem.*, **237**, 197, 335 (1938).