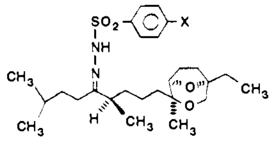
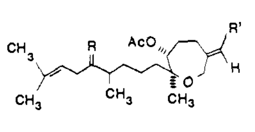


11 X = Br

12 X = CH_3



13 R = O R' = CH_2OAc

14 R = $\overset{\text{OH}}{\underset{\text{H}}{<}}$ R' = CH_2OAc

15 R = $\overset{\text{OH}}{\underset{\text{H}}{<}}$ R' = CH_2OH

16 R = $\overset{\text{OH}}{\underset{\text{H}}{<}}$ R' = CHO

17 R = $\overset{\text{OH}}{\underset{\text{H}}{<}}$ R' = CO_2Me

and then cleaved with MnO_2. At this time in our work, we obtained our first crystalline compounds, the hydrazones **11** and **12** derived from the hydrogenation (Pd/C) product of **4**. An X-ray analysis of **12** led to the assignment of the absolute configuration shown (2*S*,3*R*).[13] We were now confident in portraying zoapatanol as **1** based on the chemistry involved in the conversion of **1** to **12**. A point that still remained to be established, however, was the geometry of the hydroxyethylidine group at C-6. Acetylation (Ac_2O, pyr) of **1** afforded the diacetate **13**, which was reduced with $NaBH_4$ to the hydroxy compound **14**. Selective hydrolysis (K_2CO_3, H_2O, MeOH) of **14** afforded the primary alcohol **15**, which upon oxidation with MnO_2 gave the aldehyde **16**. Oxidation (NaCN, MnO_2, MeOH)[14] of **16** gave the desired carboxylic ester **17**. The NMR spectrum of **17** showed a signal at δ 4.17 for the 7-CH_2, while the corresponding signal in several related primary alcohols appeared at $\delta \sim 4.11$. This difference in chemical shift was consistent with the 6*E* configuration, since a downfield shift of 0.4-0.6 ppm would be anticipated for a methylene group in close proximity (6*Z*) to the anisotropic ester carbonyl.[15] Since the method for converting **1** to **17** was stereoretentive at C-6, the structure of zoapatanol was now firmly established. The structure of montanol ($C_{21}H_{36}O_4$, **2**) was established by studies similar to those conducted with **1**.

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(2) Caballero, Y.; Walls, F. *Bol. Inst. Quim. Univ. Nac. Auton. Mex.* **1970**, *22*, 79–102. These authors obtained kaurene and kaurenoic acid along with two new products, monoginoic acid and a sesquiterpene lactone (zoapatlin), from the plant roots.

(3) Geissman, T. A., and Griffin, T. S. (*Rev. Latinoam. Quim.* **1971**, *2*, 81–83) isolated and identified a sesquiterpene lactone, tomentosin, from leaves and flowers of zoapatle.

(4) The progress of our isolation work was monitored by evaluation of test substances (extracts, column fractions, and purified compounds) in pregnant guinea pigs and observation of resorption and/or abortion. Details of the biology will be forthcoming.

(5) For a detailed description of the isolation procedure, see Wachter, M. P.; Kanojia, R. M. U.S. Patent 4 086 358, April 25, 1978.

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Preparation and Properties of Molybdenum- and Tungsten-Dinitrogen Complexes. 10.[1] Conversion of Ligating Dinitrogen into Hydrazine with Hydrazido(1−) Complexes as Intermediates

Sir:

The protonation reactions of ligating dinitrogen in molybdenum and tungsten complexes have been receiving much attention in relevance to nitrogen fixation. Previously Chatt and his co-workers[2] reported that the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ or *trans*-$[M(N_2)_2(PPh_2Me)_4]$ (M = Mo or W) give, on treatment with sulfuric acid in methanol at room temperature and then base distillation for M = Mo, high yields of ammonia, together with a little hydrazine for M = W and a trace for M = Mo. The yield of ammonia is essentially 2 mol/metal atom for M = W, but only ~0.66 mol/metal atom for M = Mo.

We have recently found new protonation reactions which lead to the production of moderate yields of hydrazine in preference to ammonia from ligating dinitrogen in the tungsten complexes.[1] The reactions have now been applied to the molybdenum complexes. In a typical reaction, HCl gas was bubbled through a suspension of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ or $[MoX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl or Br) in 1,2-dimethoxyethane for several minutes at room temperature. After being stirred for ~20 h, the mixture was evaporated to dryness and the residue extracted with water. Potassium hydroxide solution (~40 wt %) was then added and the mixture distilled into dilute sulfuric acid. The yields of ammonia and hydrazine are given in Table I, which were determined by using indophenol and *p*-dimethylaminobenzaldehyde reagents, respectively. It is of great interest to note that the ligating dinitrogen on molybdenum is converted into hydrazine in moderate yields in these reactions and the nitrogen atom greater than one per molybdenum atom seems to be protonated to give hydrazine and ammonia. This is in sharp contrast to the protonation reactions reported by Chatt and his co-workers (vide supra).[2,3] They proposed the disproportionation of the N_2H_2 ligand at the hydrazido(2−) stage of reduction as in the equation $3N_2H_2 \rightarrow 2NH_3 + 2N_2$ in the case of the molybdenum dinitrogen complexes, which accounted for formation of only ~0.66 mol of NH_3/molybdenum atom. However, the results obtained here indicate that there is no substantial difference between the protonation reactions of the molybdenum- and tungsten-dinitrogen complexes, and the N_2H_2 ligand in both

Table I. Yields[a] of N_2H_4 and NH_3 on Acid Treatment

complex	acid	solvent	N_2H_4	NH_3
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$[b]	H_2SO_4	MeOH	trace	0.64
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	HCl	DME	0.32	0.31
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$[b]	H_2SO_4	MeOH	0.01	0.67
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	HCl	DME	0.52	0.24
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	HCl	DME	0.48	0.31
cis-$[W(N_2)_2(PMe_2Ph)_4]$[b]	H_2SO_4	MeOH	0.02	1.86
cis-$[W(N_2)_2(PMe_2Ph)_4]$[c]	HCl	DME	0.63	0.22
$[WBr_2(NNH_2)(PMe_2Ph)_3]$[b]	H_2SO_4	MeOH	0.06	1.72
$[WBr_2(NNH_2)(PMe_2Ph)_3]$[c]	HCl	DME	0.64	0.05
$[WClBr(NHNH_2)(PMe_2Ph)_3]Br$	HCl	DME	0.55	0.50
	H_2SO_4	DME	0.30	0.45
$[WClBr(NHNH_2)(PMe_2Ph)_3][BPh_4]$	HCl	DME	0.53	0.32

[a] Moles/gram-atom of M (M = Mo, W). [b] Reference 3. [c] Reference 1.

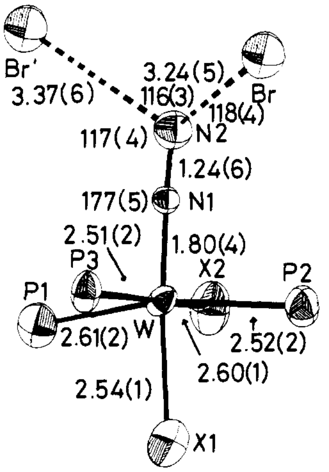

Figure 1. Perspective view of $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions. The positions indicated by X are occupied by Cl or Br atoms with the same probability. Br′ is the anion of the neighboring molecule. The angles of P(1)-W-P(3), P(1)-W-X(2), P(2)-W-P(3), and P(2)-W-X(2) are 90 (1), 79 (1), 115 (1), and 78 (1)°, respectively.

complexes is further protonated to produce predominantly hydrazine on treatment with HCl in 1,2-dimethoxyethane.

In the course of our studies of these protonation reactions, several new complexes containing the MN_2H_3 moiety have been isolated. Treatment of a suspension of the hydrazido(2−) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ in 1,2-dimethoxyethane with 1 molar equiv of HCl gas at room temperature affords an orange-yellow crystalline compound in a good yield. Analytical data are consistent with the formula $[WClBr_2(N_2H_3)(PMe_2Ph)_3]$.[4] The infrared spectrum of a chloroform solution of the complex exhibits a weak band at 3320 and a strong band at 2950 cm^{-1} assigned to ν(N-H). The ^1H NMR spectrum has resonances in CD_2Cl_2 at 9.9 (br s, intensity 2 H) and 9.8 ppm (q,[5] intensity 1 H, $^3J_{P-H}$ = ~82 Hz), which are assigned to W-NH-N*H* (β) and W-N*H*-NH (α) protons, respectively. The β-N-H exchanges immediately on addition of D_2O, whereas the α-N-H, if it exchanges, does so very slowly. Slow exchange is characteristic of such α protons.[6,7] Preliminary X-ray analysis of the complex[8] revealed that one of the two bromide ions originally coordinated to tungsten transfers from the inner coordination sphere in the reaction and the chloride ion is instead bound to the metal as shown in Figure 1. Furthermore there is a strong hydrogen-bonding interaction between the N_2H_3 group and two bromide anions, one of which is in another complex cation. A very low conductivity (0.5 cm^2/Ωmol) observed of a solution of this complex in CH_2Cl_2 indicates that strong hydrogen bonding exists even in the solution, causing the shift of the NH_2 resonance to low field and of the ν(N-H) to very low frequencies with a strong intensity (vide supra). Thus, the reasonable formulation of this complex is a hydrazido(1−) complex, $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$. Very recently Chatt and his co-workers[3,9] reported a similar strong hydrogen-bonding interaction between the NNH_2 group and the halide anions in the hydrazido(2−) complexes such as $[WBr(NNH_2)(NC_5H_4Me\text{-}4)(PMe_2Ph)_3]Br$ and $[W(NNH_2)(quin)(PMe_2PH)_3]I$. However, we can not at present preclude the possibility that the complex is formulated as a hydrazinium complex, $[WClBr(NN^+H_3)(PMe_2Ph)_3]Br^-$, in the solid state since the W-N-N linkage is rather linear, indicating three hydrogen atoms bonded to the terminal nitrogen atom.

In this complex one of the two bromide anions is very labile and, by anion exchange with an excess of $NaBPh_4$ in tetrahydrofuran-CH_2Cl_2 (1:1), another hydrazido(1−) complex, $[WClBr(NHNH_2)(PMe_2Ph)_3][BPh_4]$, is obtained.[10] The complex is characterized by three bands in the infrared spectrum at 3320, 3200, and 3105 cm^{-1} assigned to ν(N-H). The hydrazido(1−) complex $[WCl_3(NHNH_2)(PPh_2Me)_2]$ which was recently prepared by the reaction of *trans*-$[W(N_2)_2(PPh_2Me)_4]$ with HCl gas in CH_2Cl_2 exhibits similar bands in the same region.[6] The ^1H NMR spectrum gives rise to resonances at 3.6 (br s, intensity 2 H) and 9.3 ppm (q,[5] intensity 1 H, $^3J_{P-H}$ = 82 Hz) which are assigned to β and α protons, respectively. Since an anion, $[BPh_4]$, is not capable of strong hydrogen bonding, the NH_2 resonance appears at relatively high field.

Speculation on the mechanism for formation of the former hydrazido(1−) complex must await further investigations. However, the coordination of chloride anion in the inner coordination sphere (vide supra) suggests that the hydrazido(2−) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ is first attacked by a chloride anion. Then the NNH_2 ligand as a formal 4-electron donor adjusts itself to become the NH=NH ligand as a formal 2-electron donor and the complex adopts an 18-electron system, which is followed by the protonation on the terminal nitrogen and transfer of a bromide anion into the outer coordination sphere owing to a steric effect to give the hydrazido(1−) complex $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$.

The results of acid treatment of the hydrazido(1−) complexes obtained here are shown in Table I. Treatment of $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$ with HCl in 1,2-dimethoxyethane produces hydrazine in preference to ammonia, and their yields are similar to those obtained from the parent hydrazido(2−) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ on treatment with an excess of HCl in 1,2-dimethoxyethane. This indicates that the M-NHNH$_2$ stage of reduction is on the route to hydrazine. Hydrogen chloride seems to be a better acid for converting the ligating dinitrogen into hydrazine compared with H_2SO_4. Further investigations are now in progress to understand subtle factors which determine the reduction course of ligating dinitrogen to ammonia or hydrazine.

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(5) The spectrum does not show a clear quartet since the spin–spin coupling constants $^3J_{P(1)-H}$, $^3J_{P(2)-H}$, and $^3J_{P(3)-H}$ (see Figure 1) are slightly different. Interpretation on the fine structures observed in each peaks must await further investigations.

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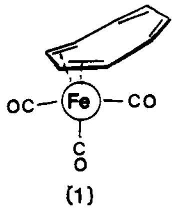
Structural Consequences of Electron-Transfer Reactions. 3.[1] Electrochemical Isomerization of a Metal-Hydrocarbon Bond in the Reduction of Cyclopentadienylcobalt Cyclooctatetraene

Sir:

Geometrical preferences of polyolefins bonded to metals are of importance to catalytic processes involving organometallic compounds and intermediates. We report electrochemical and NMR data showing that cyclooctatetraene (COT) may bond either as a 1,3 diolefin or 1,5 diolefin to cobalt in the π compound (COT)CoCp (Cp = η^5-C_5H_5), in an equilibrium mixture. Furthermore, the thermodynamically favored 1,5 compound rapidly and quantitatively isomerizes to the 1,3 compound when it is reduced by one electron. This appears to be the first known example of a *reversible electrochemical isomerization* of a metal-hydrocarbon bond.

The ways in which the polyolefin cyclooctatetraene may bond to a metal are manifold and have been the subject of much discussion.[2-5] Interestingly, the ligand bonds as a conjugated 1,3 diolefin to tricarbonyliron (**1**),[6] but has been reported to bond as a nonconjugated 1,5 diolefin to η^5-cyclopentadienylcobalt (**2**).[3,7] However, our electrochemical experiments indicated the presence of two species, in equilibrium, in solutions of samples of carefully purified (**2**).[8] Cyclic voltammetry (CV) measurements of the reduction of nominal **2** in nonaqueous solvents such as THF or CH_3CN[9] showed two reduction waves (A, e_{p_c} = −1.84; B, e_{p_c} = −2.07 V) and one oxidation wave (C, e_{p_a} = −1.78 V) in the region of interest (Figure 1). Waves A and C form a reversible couple, as scans reversed at the foot of wave B demonstrate (Figure 1). When the scan is negative enough to include reduction B, oxidation wave C is greatly enhanced. As the temperature was lowered, the height of wave B increased at the expense of wave A, but the oxidation current C remained the same (corrected, of course, for changes in diffusion rate). The temperature effects were completely reversible, and the total reduction current corresponded to passage of one electron. Thus, species A and B are in equilibrium, with B being the thermodynamically more stable isomer. However, the anion of B is very unstable, and rapidly forms the radical anion of A, which is reoxidized at −1.78 V.



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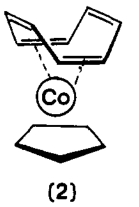

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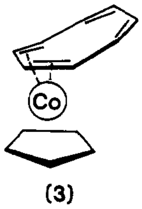

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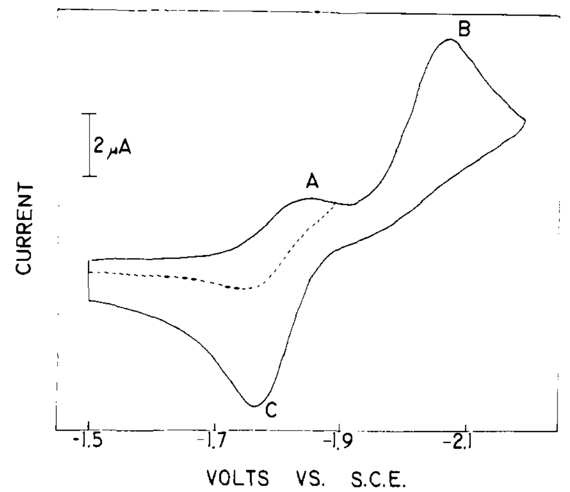

Figure 1. Cyclic voltammogram of (COT)CoCp in THF-0.1 M Bu_4NPF_6 at a hanging mercury drop electrode. Dotted line shows result of scan in which potential was reversed prior to onset of wave B. Scan rate = 500 mV/s.

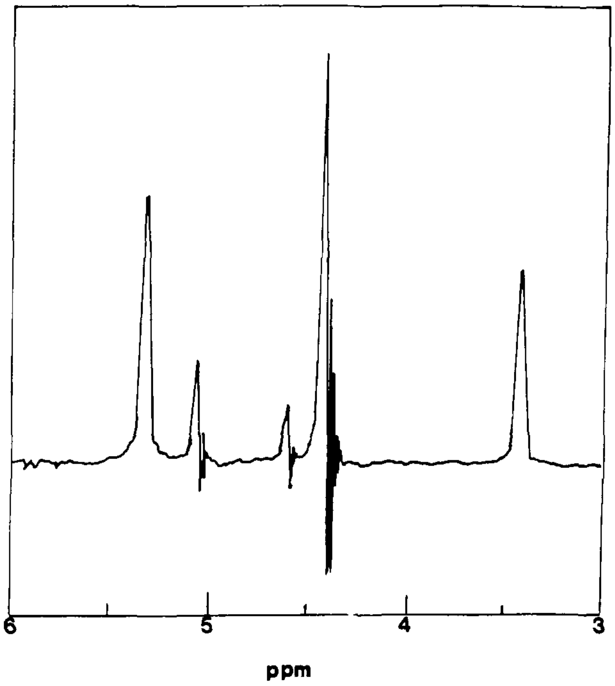

Figure 2. 60-MHz ^1H NMR spectrum of (COT)CoCp in hexane at 20 °C. Chemical shifts are reported as δ values.

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