114033-33-9; NaCH(CO$_2$Me)$_2$, 18424-76-5; [CpRu(BT-d_2)]PF$_6$, 114033-35-1; CpRu(NCMe)$_3$PF$_6$, 84987-57-5; [Cp*Ir(BT-d_2)](BF$_4$)$_2$, 114033-37-3; PPN[HFe(CO)$_4$], 56791-54-9; [Cp*Ir(BT·PPh$_2$Me)]$^{2+}$, 114057-39-5; [Cp*Ir(T)](BF$_4$)$_2$, 112068-91-4; [Cp*Ir(T·PMe$_3$)]$^{2+}$, 114033-38-4; [Cp*Ir(T·PPh$_2$Me)]$^{2+}$, 114033-39-5; [Cp*Ir(T·PPh$_3$)]$^{2+}$, 114033-40-8; [Cp*Rh(T)](PF$_6$)$_2$, 112068-87-8; [Cp*Ir(T·P(O)(OMe)$_2$)]BF$_4$, 114033-42-0; [Cp*Rh(T·PMe$_3$)](BF$_4$)$_2$, 114033-44-2; Cp*Ir(η^4-T), 114057-40-8; Cp$_2$Co, 1277-43-6; [Cp*Rh(BT)](PF$_6$)$_2$, 112068-89-0.

Supplementary Material Available: Tables of least-squares planes for 6 and ^{1}H NMR data for all isomers of complexes 2–13 (6 pages); a listing of structure factors for 6 (11 pages). Ordering information is given on any current masthead page.

EPR Studies of the 1,2-Diketone Chelate Paramagnetic Complexes Produced in the Photochemical Reactions of Hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, [CpMo(CO)$_3$]$_2$, and 1,2-Diketones

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Received August 12, 1987

The paramagnetic products generated in the photochemical reaction of hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, [CpMo(CO)$_3$]$_2$, with a series of 1,2-diketones have been examined by the EPR spectroscopy. The observed paramagnetic products are shown to have a structure in which the 1,2-diketone chelates to Mo in CpMo(CO)$_2$, which is produced by photocleavage of the Mo–Mo bond and subsequent elimination of one of the carbonyl groups. The series of the complexes show marked changes of the spin distribution in the molecules with the 1,2-diketone ligands; i.e., in some cases most of the unpaired spin is distributed on the 1,2-diketone ligand, while in other cases the spin is distributed mainly on the fragment Mo(CO)$_2$$^{2+}$. The isotropic g values and Mo hyperfine (hf) coupling constants change with the spin distribution in the complexes, and a good correlation was observed between the g and Mo hf coupling values. The change of the spin densities on the 1,2-diketone ligands correlate well with the orbital energies of LUMO's of the 1,2-diketones.

Introduction

The chemical reactivity of metal carbonyl complexes containing a metal–metal bond has been the subject of extensive study. It has been shown that photolytic cleavage of the metal–metal bonds commonly occurs and the resulting paramagnetic species undergo various reactions.[2,3] Although the paramagnetic intermediates are too reactive to be detected directly by EPR, they are known to be trapped by quinones or 1,2-diketones to form moderately stable paramagnetic complexes.[4-15] The structure and electronic configuration of these complexes are interesting because both the central metal and the 1,2-diketone ligands can accept the unpaired electron.

Hexacarbonylbis(η^5-2,4-cyclopentadien-1-yl)dimolybdenum, [CpMo(CO)$_3$]$_2$, has a Mo–Mo bond,[16] and cleavage of the bond occurs by the near-UV and visible photoirradiation with a high quantum yield.[17,18] Though [CpMo(CO)$_3$]$_2$ has been shown to undergo photochemical reactions with di-*tert*-butyl-1,2-benzoquinones, *o*-chloranil, and fluorinated 1,2-diketones to yield paramagnetic products,[11,12] details of the structures of the products are not known. Few reports have appeared on paramagnetic products containing the cyclopentadienyl group. In the present work, we examine the photochemical reactions of [CpMo(CO)$_3$]$_2$ with a series of 1,2-diketones involving *o*-quinones and

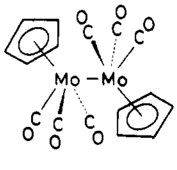

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Table I. EPR Parameters for the 1,2-Diketone Chelate Complexes for $CpMo(CO)_2$, $CpMo(CO)(PPh_3)$, and the 1,2-Diketone Anion Radicals

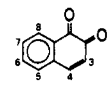
1,2-diketone	metal or counterion	solvent	*g* value	a_{Mo}/G	a_H/G[a]
NQ	$CpMo(CO)_2$	toluene	1.9932	13.7	$a_{H^4} = 2.0$
	$(n\text{-}Bu)_4N^+$	DMF[b]	2.0048	...	$a_{H^4} = 3.9$, $a_{H^6} = 1.5$, $a_{H^8} = 1.0$, $a_{H^3} = 0.4$, $a_{H^5} = 0.3$
PQ	$CpMo(CO)_2$	toluene	1.9957	11.2	$a_{H^{1,3,6,8}} = 1.0$ (4 H), $a_{^{13}C} = 1.9$ (2 C)[e]
	$(n\text{-}Bu)_4N^+$	DMF[b]	2.0049	...	$a_{H^{3,6}} = 1.67$ (2 H), $a_{H^{1,8}} = 1.34$ (2 H), $a_{H^{4,5}} = 0.42$ (2 H), $a_{H^{2,7}} = 0.21$ (2 H)
FR	$CpMo(CO)_2$	toluene	1.9975	8.6	$a_{H^{1,3}} = 1.2$ (4 H)
	$(n\text{-}Bu)_4N^+$	DMF[b]	2.0048	...	$a_{H^3} = 2.0$ (2 H), $a_{H^1} = 1.5$ (2 H), $a_{H^2} = 0.35$ (2 H)
BZ	$CpMo(CO)_2$	toluene	1.9979	8.8	...
	$(n\text{-}Bu)_4N^+$	DMF[b]	2.0050	...	$a_{H^p} = 1.1$ (2 H), $a_{H^o} = 1.0$ (4 H), $a_{H^m} = 0.35$ (4 H)
PPD	$CpMo(CO)_2$	toluene	1.9985	7.6	$a_{H^{Me}} = 4.2$ (3 H)
	K^+	DMSO/*tert*-butylalcohol (4:1)[c]	...	...	$a_{H^{Me}} = 3.43$ (3 H), $a_{H^p} = 1.84$, $a_{H^o} = 1.59$ (2 H), $a_{H^m} = 0.53$ (2 H)
DA	$CpMo(CO)_2$	toluene	1.9998	6.1	$a_{H^{Me}} = 5.8$ (6 H)
	K^+	DMSO[d]	2.00483	...	$a_{H^{Me}} = 7.0$ (6 H)
AQ	$CpMo(CO)_2$	toluene	2.0003	5.0	$a_{H^{3,5,6,8}} = 1.0$ (4 H), $a^{13}{}_C = 0.5$ (2 C)[e]
	$CpMo(CO)(PPh_3)$	toluene	1.9960	11.8	$a^{31}{}_P = 5.7$
	$(n\text{-}Bu)_4N^+$	DMF[b]	2.0047	...	$a_{H^{3,5,6,8}} = 1.2$ (4 H), $a_{H^{4,7}} = 0.25$ (2 H)
DTBQ	$CpMo(CO)_2$	toluene/pentane (1:2)[f]	1.990	15.6	$a_{H^{4,5}} = 1.0$ (2 H)
	Na^+	water/EtOH[g]	...	...	$a_{H^{4,5}} = 3.3$ (2 H)

[a] The number of equivalent protons is indicated in parentheses. [b] The anion radical is produced by electrolytic reduction. [c] Reference 20. The value for the radical having a trans C=O—C=O configuration. [d] Reference 21. [e] The hyperfine (hf) coupling constant of ^{13}C in carbon monoxide. [f] Reference 11. [g] Reference 22.

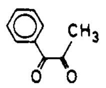
elucidate the structural details of the paramagnetic products by EPR spectroscopy.

Experimental Section

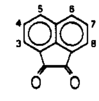
$[CpMo(CO)_3]_2$ was commericially obtained from Strem Chemicals and used as received. Toluene was used as a solvent; it was dried by distillation over molecular sieves in a vacuum line. 1,2-Naphthoquinone (NQ), 1,2-acenaphthenequinone (AQ), and 9,10-phenanthrenequinone (PQ) were vacuum sublimed before use. 1-Phenyl-1,2-propanedione (PPD) and diacetyl (DA) were distilled over molecular sieves in the vacuum line. Furil (FR), benzil (BZ), and triphenylphosphine (PPh_3) obtained commercially as the best available grade were used without further purification.



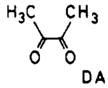
NQ



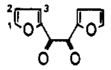
PPD



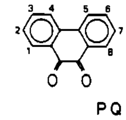
AQ



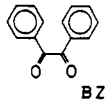
DA



FR



PQ


BZ

$[CpMo(^{13}CO)_3]_2$ was synthesized from $[CpMo(CO)_3]_2$ by the photosubstitution of CO with ^{13}CO under ^{13}CO atmosphere[19] in toluene. Almost complete substitution by ^{13}CO's was confirmed by the mass spectra.

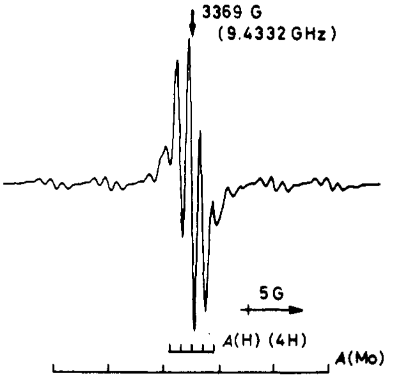


Figure 1. First-derivative X-band EPR spectrum observed after photoirradiation of a toluene solution containing $[CpMo(CO)_3]_2$ and AQ at room temperature.

Typical sample solutions contain $[CpMo(CO)_3]_2$ (0.4 mg, 8.1 × 10^{-7} mol) and the 1,2-diketone (ca. 2 equiv mol for $[CpMo(CO)_3]_2$) in 0.6 cm^3 of toluene and were prepared in a vessel connected to a 5-mm o.d. quartz tube and degassed in vacuo. The solutions were kept at liquid-nitrogen temperature until just before photolysis. The solution in the quartz tube was cooled below room temperature and irradiated in situ in an EPR cavity with a 100-W high-pressure mercury lamp equipped with a remote-controlled shutter. The temperature and irradiation time were set so as to enable the EPR observation of the products most efficiently. No appreciable differences were observed for different ratios of $[CpMo(CO)_3]_2$ to 1,2-diketones. Ligand substitution by PPh_3 was accomplished by adding PPh_3 to the sample solutions before photoirradiation.

For comparison, EPR spectra of 1,2-diketone anion radicals were examined. The anion radicals were prepared by electrochemical reduction in dimethylformamide (DMF) using tetra-*n*-butylammonium perchlorate as the supporting electrolyte.

EPR spectra were recorded on a JEOL JES-FE2XG X-band spectrometer using 100-kHz field modulation. The temperature was controlled by standard accessories. The microwave frequency was monitored with a Takedariken TR-5501 frequency counter equipped with a TR-5023 frequency converter. The magnetic field was measured with a Echo electronics EFM-2000 NMR oscillator.

Results and Discussion

Irradiation of a toluene solution containing $[CpMo(CO)_3]_2$ and AQ gave an EPR spectrum (Figure 1) that exhibits a strong center absorption and six weak satellites

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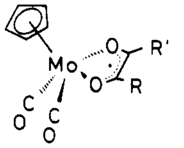
arising from the hyperfine (hf) interaction with the magnetic isotopes ^{95}Mo (15.8%, $I = {}^5/_2$, $\mu = -0.9099\ \mu_N$) and ^{97}Mo (9.6%, $I = {}^5/_2$, $\mu = -0.9290\ \mu_N$). Each component of the spectrum was further resolved into a quintet by the interaction of the electron with four-equivalent protons.

EPR spectra showing a similar Mo satellite pattern were observed in photochemical reactions between $[CpMo(CO)_3]_2$ and NQ, PQ, FR, BZ, PPD, or DA. The EPR parameters obtained from these reaction products are listed in Table I together with the data for the anion radicals of the corresponding 1,2-diketones for comparison. In the case of the paramagnetic product with BZ, a spectrum with a broad line width showing no further hf splittings was observed, but in the other cases, the products showed well-resolved hf structures apparently due to the interaction with protons. The features of the observed proton hf splittings correspond well to those of the 1,2-diketone anion radicals and hence can be assigned to interactions with the 1,2-diketone protons. The paramagnetic products observed above are therefore considered to be adducts of $CpMo(CO)_3$ produced by the photolytic cleavage of the Mo–Mo bond and the 1,2-diketones.

In order to elucidate the structure of these paramagnetic complexes, we attempted to observe EPR spectra of the complexes derived from $[CpMo(CO)_3]_2$ involving carbon-13 enriched carbon monoxide. The paramagnetic complexes produced by the photochemical reaction of $[CpMo(^{13}CO)_3]_2$ with PQ and AQ exhibited EPR spectra having an additional triplet hf structure besides the splittings due to the interactions with Mo and protons, and this triplet hf coupling can be assigned to the interaction with two ^{13}C nuclei in the complexes. This clearly indicates that the complexes have two equivalent CO's (Table I). From these facts the paramagnetic complexes are considered to be formed from $CpMo(CO)_2$ and 1,2-diketones having a structure where Mo is chelated by the two carbonyl oxygens of the 1,2-diketones as shown:



In these complexes, a rapid equilibrium between unsymmetrical structures, in which the 1,2-diketones coordinate to Mo by one carbonyl oxygen, is ruled out because the complexes apparently have only two CO's and no line-width broadening effect caused by the exchange reaction was observed over a wide temperature range (room temperature to −80 °C). The chelated structure has been also reported for the complex of Mo and *o*-chloranil which was formed by the reaction of $Mo(CO)_6$ with *o*-chloranil.[23]

As mentioned above, the proton hf coupling constants correspond well to those of 1,2-diketone anion radicals. In some cases they are nearly the same in magnitude as those for the corresponding anion radicals. These facts indicate that the paramagnetic center in these complexes is mainly on the 1,2-diketone ligands and the unpaired electron on the ligands mainly occupies its π LUMO as in the 1,2-diketone anion radicals. Such electronic configuration in the ligands satisfies the 18-valence electron rule for the electronic configuration of the central metal and explains well the moderately high stability of the complexes.

Sarbasov et al. investigated the photochemical reaction of $[CpMo(CO)_3]_2$ with 3,6-di-*tert*-butyl-1,2-benzoquinone (DTBQ) and reported the formation of a paramagnetic complex, $CpMo(CO)_2(DTBQ)$.[11] They proposed that Mo takes the 4d^3 configuration and the quinone chelates to Mo as the pyrocatechol ligand. However, in the present case, it is reasonable to propose that the quinones have the semiquinone form in the complexes.

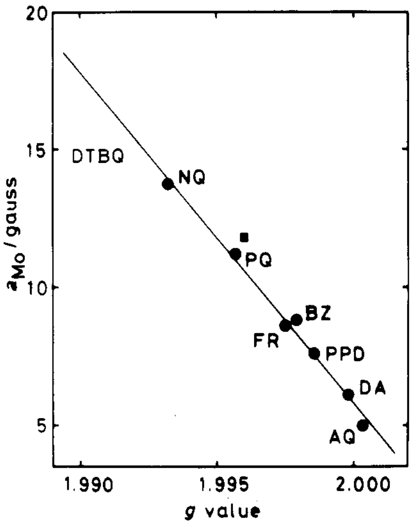
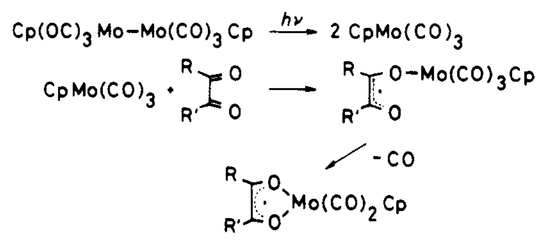


Figure 2. Plots of a_{Mo}'s vs g values of the complexes $CpMo(CO)_2$(1,2-diketone) (●), $CpMo(CO)(PPh_3)(AQ)$ (■), and $CpMo(CO)_2(DTBQ)$ (○) from ref 11.

Scheme I



It has been shown that $[CpMo(CO)_3]_2$ primarily undergoes photocleavage of the Mo–Mo bond, producing the $CpMo(CO)_3$, which is trapped by a spin trap reagent, 2,3,5,6-tetramethyl-1-nitrosobenzene,[24] or reacts with carbon tetrachloride yielding $CpMo(CO)_3Cl$.[17] In view of these facts, the reactions of $[CpMo(CO)_3]_2$ with the 1,2-diketones may be written as shown in Scheme I.

Photoirradiation of the toluene solution containing $[CpMo(CO)_3]_2$, AQ, and PPh_3 gives an EPR spectrum exhibiting hf splittings due to the interaction with ^{31}P in addition to Mo and AQ protons. The complex produced by this photochemical reaction therefore may be assigned to $CpMo(CO)(PPh_3)(AQ)$, where one of the carbon monoxides is further substituted by PPh_3.[5,9,13,25]

In the case of NQ complex, which shows the largest Mo hf coupling among the products, the observed ligand proton hf coupling constant is roughly half the coupling constant of the corresponding proton in the NQ anion radical. This indicates that roughly 50% of the unpaired electron density is on the NQ ligand and rest is delocalized onto the other part of the molecule. In view of the fact that there is no indication of hf interaction with the cyclopentadienyl protons, while the ^{13}CO-substituted complexes show ^{13}C hf couplings, the unpaired electron may

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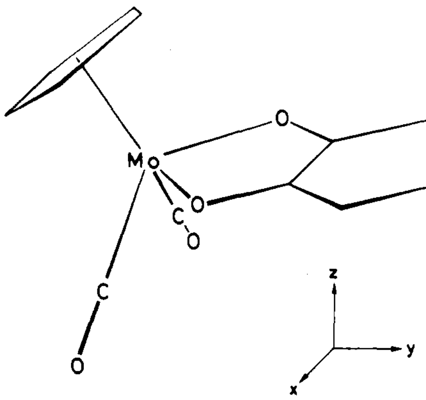

Figure 3. Structure of a model complex, $CpMo(CO)_2(BQ)$, for the EHMO calculation: $r_{Mo-O} = 2.00$ Å; $r_{Mo-C(CO)} = 1.97$ Å; $r_{C-C(Cp)} = 1.43$ Å; $r_{C-O(CO)} = 1.14$ Å; $r_{C-C} = 1.40$ Å; $r_{C-O} = 1.30$ Å; $r_{C-H} = 1.09$ Å. The distance from Mo to the Cp plane = 2.00 Å. BQ is on the *xy* plane, and the CO's are on the *xz* plane. The angle C(CO)–Mo–C(CO) = 90°. The normal of Cp is on the *yz* plane, and the angle between the normal and the *y* axis is 125.3°.

reside on the $Mo(CO)_2^{2+}$ fragment. In the complexes showing smaller Mo hf couplings, the proton hf coupling constants of the 1,2-diketone ligands are closer to those of the corresponding 1,2-diketone anion radicals, and hence more unpaired electron density is thought to be on the 1,2-diketone ligands.[26]

The *g* values of the complexes deviate from the free spin value, and the deviations correlate with the Mo hf coupling constants as shown in Figure 2. The deviations of the *g* values are mainly due to the effect of spin–orbit coupling of the unpaired electron residing on the Mo atom, which has the largest spin–orbit coupling constant among the atoms constituting the complexes. Therefore, a larger spin density on Mo, which is indicated by a larger Mo hf coupling constant, is expected to give a larger deviation of the *g* value, as is shown by the good correlation between the *g* values and the Mo hf coupling constants. It should be noted that changes in *g* values with 1,2-diketones are large compared to those in other metal carbonyl complexes with 1,2-diketone ligands.[6,9,15] We know of no cases showing such large changes of *g* values with 1,2-diketone ligands. This can be attributed to the marked changes in spin distribution that occurs with the 1,2-diketone ligands, as is apparent from the ligand proton hf couplings, showing that there are cases in which about 50% of the unpaired electron delocalize on the $Mo(CO)_2^{2+}$ fragment and other cases in which most of the unpaired electron resides on the 1,2-diketone ligands.

We attempted to correlate the unpaired electron distribution with the nature of the π electronic structure of the 1,2-diketone ligands by the MO method. The calculations were done for a model complex, $CpMo(CO)_2(BQ)$ (BQ = *o*-benzoquinone), and the complexes with NQ, PQ, and AQ by the extended Hückel method with "weighted" H_{ij}'s.[27] The parameters used in the calculations were taken from the literature.[28] The complexes were assumed to have the C_s symmetry, as shown in Figure 3, but for convenience they were divided into two parts, $CpMo(CO)_2^+$ and the quinone anion radicals, for the calculations.

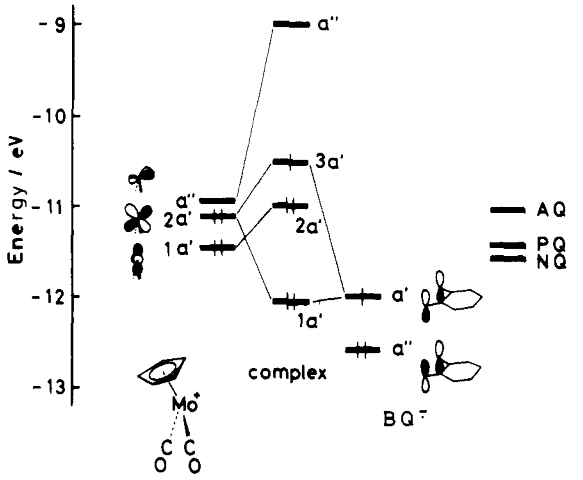

Figure 4. The orbital interaction diagram for $CpMo(CO)_2^+$ and the BQ anion radical. The LUMO's of AQ, PQ, and NQ are also illustrated on the right side.

The frontier orbitals of the metal fragment $CpMo(CO)_2^+$ and the π orbitals of BQ are shown in Figure 4. The orbitals a′ are symmetrical to the *yz* plane, and the orbitals a″ are antisymmetrical. The orbitals of the metal fragment agree well with those reported by Schilling et al.[28b] The LUMO of BQ is symmetrical about the two carbonyl groups and overlaps with 2a′ in the metal fragment where the main metal orbital is d_{yz}. These two orbitals form the SOMO of the paramagnetic complex. The LUMO's of the other quinones have the same symmetry as that in BQ, and the SOMO of the complexes are thought to be formed in the same manner. The orbital levels of the LUMO's of NQ, PQ, and AQ are also indicated in Figure 4.

The spin distribution between the metal fragment and the 1,2-diketone ligand in the complex depends on the relative height of the orbital energies of 2a′ in the metal fragment and of the LUMO in the 1,2-diketone ligand. Since the SOMO is formed by antibonding combination of these two orbitals, the contribution of the LUMO of the 1,2-diketone ligand to the SOMO becomes larger by energy elevation of the LUMO, and hence it leads to the smaller spin density on the metal fragment. As Figure 4 shows, the LUMO's of NQ, PQ, and AQ elevate in this order, and spin densities on the ligands are expected to increase in this order. This expectation is consistent with the observed changes in the spin densities on the ligands. In the present case, as the 2a′ of the metal fragment is at a comparable height to the levels of the 1,2-diketone LUMO's, changes in the orbital energies of the ligand LUMO's will markedly affect the spin distribution in the molecules.

In the complex, the nearest orbital to the SOMO is 2a′, which is situated below the SOMO, and the energy level of a″ of the metal fragment elevates largely by interaction with the quinone σ orbitals. However, almost all orbitals have a large component of the metal d orbitals situated above the SOMO. The observed negative *g* shift from the free spin value indicates that the mixing of the SOMO with such vacant orbitals including a″ is making a more important contribution to the *g* shift rather than the mixing with 2a′.

The metal d_{yz} orbital, which overlaps with the LUMO's of the 1,2-diketone ligands, also overlaps with the π orbitals of the carbon monoxides. The EHMO calculation shows that the π orbitals of the carbon monoxides contribute appreciably to the 2a′ orbital of the metal fragment, and hence the unpaired spin is expected to delocalize effectively

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(26) The chelated PPD shows a larger a_H^{Me} value than that in the corresponding free anion radical. This may be attributed to the fact that PPD in these two systems have configurations different from each other; the chelated PPD has a cis C=O—C=O configuration while the free anion has a trans.

(27) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(28) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

from the 1,2-diketone ligand onto the CO π orbitals through the metal d_{yz} orbital. Such spin delocalization is evidenced by the observed ^{13}CO hf couplings. The calculation also shows that the spin delocalization onto the cyclopentadienyl group is very small, consistent with the experimental results showing no hf splittings due to the group.

Previously, Sarbasov et al. reported that the CpMo(CO)$_2$(DTBQ) complex has most of its unpaired electron on Mo. They explained it by assigning the 4d^3 configuration to Mo and by assuming that DTBQ is coordinated to Mo as the pyrocatecholate ligand.[11] Their g and Mo hf coupling values fit on the correlation line of Figure 2 obtained for the complexes in this work. The orbital energy of the LUMO of BQ is much lower than those for AQ, PQ, and NQ (Figure 4), and hence on the basis of the reason mentioned above, the unpaired electron in the DTBQ complex is expected to be delocalized more onto the metal fragment than in the other 1,2-diketone complexes. The Sarbasov et al.'s complex, therefore, may be thought to have the same electronic configuration as in the present case. It seems interesting that in the CpMo(CO)$_2$(1,2-diketone) complexes the spin distribution is markedly affected by 1,2-diketone ligands; i.e., the spin distribution changes from the case where most of the spin is distributed on the 1,2-diketone ligand to the case where the spin is mainly distributed on the metal fragment.

Acknowledgment. This work was partly supported by the joint studies program (1985) of the Institute for Molecular Science, Okazaki.

Registry No. NQ, 524-42-5; AQ, 82-86-0; PQ, 84-11-7; PPD, 579-07-7; DA, 431-03-8; FR, 492-94-4; BZ, 134-81-6; [CpMo(CO)$_3$]$_2$, 12091-64-4; CpMo(CO)$_2$(NQ), 114532-62-6; CpMo(CO)$_2$(PQ), 114532-63-7; CpMo(CO)$_2$(FR), 114532-64-8; CpMo(CO)$_2$(BZ), 114532-65-9; CpMo(CO)$_2$(PPD), 114532-66-0; CpMo(CO)$_2$(DA), 114532-67-1; CpMo(CO)$_2$(AQ), 114532-68-2; CpMo(CO)(PPh$_3$)(AQ), 114532-69-3; (NQ)$^-$(n-Bu)$_4$N$^+$, 114550-09-3; (PQ)$^-$(n-Bu)$_4$N$^+$, 114532-58-0; (FR)$^-$(n-Bu)$_4$N$^+$, 114532-59-1; (BZ)$^-$(n-Bu)$_4$N$^+$, 114532-60-4; (AQ)$^-$(n-Bu)$_4$N$^+$, 114532-61-5; CpMo(CO)$_2$(BQ), 114532-70-6.

Synthesis of New Chiral Ferrocenyl Amine Sulfide Complexes and Their Applications as Asymmetric Catalysts. The Structure of (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SCH_3][PdCl_2]$

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Received August 25, 1987

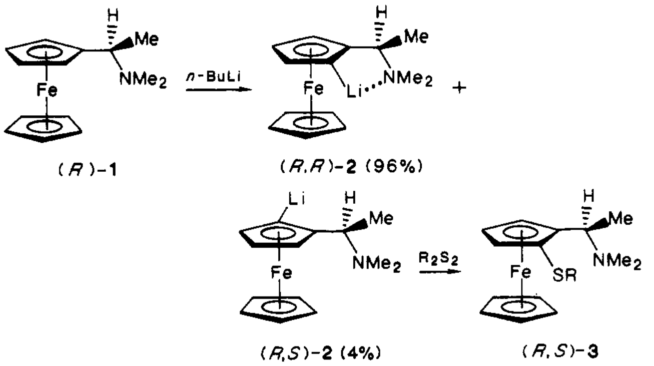
New chiral ferrocenyl sulfide ligands of the type (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]$, where R = Me, Et, i-Pr, n-Bu, i-Bu, t-Bu, i-Pent, Ph, CH$_2$Ph, p-tolyl, or 4-chlorophenyl, have been prepared by lithiation of optically active N,N-dimethyl-1-ferrocenylethylamine followed by reaction with the appropriate disulfide. These compounds are air-stable and readily chelate palladium and platinum chloride to form chiral heterobimetallic complexes (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR][MCl_2]$ (R = Me, i-Pr, n-Pr, i-Bu, Ph, p-tolyl, 4-chlorophenyl; M = Pd, Pt). Both the ligands and the complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and infrared spectroscopy. The chiral complexes are asymmetric Grignard cross-coupling catalysts. The configuration of the cross-coupling product is related to the planar chirality of the complex. The structure of (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SMe][PdCl_2]$ (15) was determined by single-crystal X-ray diffraction measurements. Compound 15 crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice parameters a = 9.226 (3) Å, b = 12.219 (4) Å, c = 15.448 (5) Å, M_r 480.56, V = 1741.5 (8) Å^3, ρ(calcd) = 1.83 g/cm^3, and Z = 4. Least-squares refinement gave a final R value of 0.029 for 2175 observed ($I > 3\sigma(I)$) of 2912 unique reflections. The two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other; the dihedral angle is 3.2°.

Introduction

Recently, we reported the synthesis of new ferrocenyl amine sulfide complexes and their catalytic applications to selective hydrogenation.[1,2] Kellogg and co-workers have also reported the catalytic application of chiral macrocyclic sulfide complexes to asymmetric Grignard cross-coupling reactions.[27] In this work, we report the synthesis of new chiral ferrocenyl sulfide ligands of the type (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]$, where R = Me, Et, i-Pr, n-Bu, i-Bu, t-Bu, i-pentyl, Ph, CH$_2$Ph, p-tolyl, or 4-chlorophenyl.

These compounds are easily prepared by the initial lithiation of the resolved amine 1 in a highly stereospecific manner,[3] followed by treatment of the major diastereomer of 2 with RSSR to afford (R,S)-3 (Scheme I). These chiral ferrocenyl amine sulfides readily chelate platinum and

Scheme I



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