J. Am. Chem. Soc. **1983**, *105*, 6980–6982

Table II. Rates of Deprotonation of $HMo(CO)_2(DPPE)_2^+BF_4^-$ (0.004 M in CH_2Cl_2) by Pyridine and Pyridine in the Presence of Additives

entry	[py], M	equiv	anion[a]	[anion], M	equiv	k_{obsd}, min^{-1} [b]	k_1, min^{-1} M^{-1} [c]
1	0.10	25				$4.14\ (\pm 0.38) \times 10^{-4}$	4.14×10^{-3}
2	0.18	35				$6.57\ (\pm 0.22) \times 10^{-4}$	3.65×10^{-3}
3	0.22	45				$7.78\ (\pm 0.26) \times 10^{-4}$	3.53×10^{-3}
4	0.26	55				$9.22\ (\pm 0.39) \times 10^{-4}$	3.55×10^{-3}
5	0.060	20	Cl^-	0.060	15	$1.18\ (\pm 0.11) \times 10^{-2}$	1.96×10^{-1}
6	0.080	20	Cl^-	0.088	22	$1.70\ (\pm 0.18) \times 10^{-2}$	1.93×10^{-1}
7	0.080	20	Cl^-	0.120	30	$2.38\ (\pm 0.10) \times 10^{-2}$	1.98×10^{-1}
8	0.020	5	Cl^-	0.080	20	$1.65\ (\pm 0.07) \times 10^{-2}$	2.06×10^{-1}
9[d]	0.080 (NEt_3)	20	Cl^-	0.080	20	$1.61\ (\pm 0.007) \times 10^{-2}$	2.01×10^{-1}
10	0.080	20	OAc^-	0.080	20	$1.00\ (\pm 0.002) \times 10^{-2}$	1.21×10^{-1}
11[e]	0.080	20	OAc^-	0.068	17	$7.56\ (\pm 0.15) \times 10^{-3}$	1.10×10^{-1}
12	0.080	20	I^-	0.080	20	$1.12\ (\pm 0.13) \times 10^{-3}$	1.40×10^{-2}
13	0.080	20	F^-	0.080	20	too rapid to measure	

[a] Added salts have the bis(triphenylphosphine)imminium, PPN^+, counterion except where indicated. [b] Obtained by a plot of ln (Abs_t–Abs_∞) vs. time over 1–2 half-lives of reaction. Error calculated at 95% confidence limit for an individual run. Reproducibility was within 5–10%. [c] Obtained by k_{obsd}/[py] for entries 1–4 and by k_{obsd}/[anion] for entries 5–12. k_1 is the second-order rate constant defined by eq 1. [d] In this run NEt_3 was used as base instead of pyridine. [e] Acetate added as the K^+·benzo-18-C-6 salt.

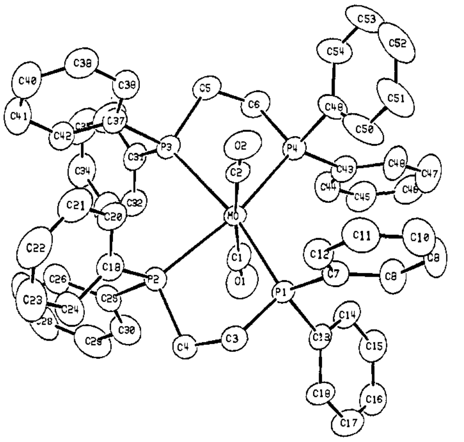

Figure 1. An ORTEP drawing of $HMo(CO)_2(DPPE)_2^+$ showing 40% probability ellipsoids. Phenyl hydrogen atoms were included in calculated positions (assuming idealized geometries with C–H = 0.95 Å) and were not refined. Pertinent bond lengths and bond angles: Mo–P1, 2.466 (1); Mo–P2, 2.574 (2); Mo–P3, 2.583 (2); Mo–P4, 2.468 (2); Mo–C1, 2.021 (8); Mo–C2, 1.900 (8) Å. P1–Mo–P4, 114.61(6)°; P2–Mo–P3, 89.62 (6)°; P3–Mo–P4, 78.28 (6)°; P1–Mo–P2, 77.8 (6)°; C1–Mo–C2, 175.4 (3)°

The ORTEP plot in Figure 1 shows the structure of the cation to be one with a trans arrangement of CO groups and the P-donor atoms to be roughly in a plane. Although refined to a (weighted) agreement factor of 0.054, the hydride was not observed in the final difference map. On examination of the MoP_4 bond angles and distances and by comparison to the structures of $HTa(CCMe_3)(Me_2PCH_2CH_2PMe_2)_2(ClAlMe_3)$[12] and $HTa(CO)_2(Me_2PCH_2CH_2PMe_2)_2$,[13] the hydride position is inferred to be between P1 and P4, in or very near the MoP_4 plane. To our knowledge this is the first example of two DPPE ligands occupying the plane of a PB structure.[14]

We have thus implicated a simple mechanism for deprotonation in which bases burrow into the $Mo–H^+$ binding site, electrostatically interact with the proton, and abstract it. There are, however, in the cationic complex additional sites for nucleophilic attack: the carbonyl carbon and the molybdenum(II) center. Base or anion interaction at these sites might reasonably be proposed to precede H^+ abstraction. Nevertheless there was found no spectroscopic evidence for formation of adducts of any type,[15] and furthermore no easy way to explain why either of the two alternate reaction (or prereaction) sites might show the observed dependence of rate on anion size.

Acknowledgment. Appreciation is expressed to the Robert A. Welch Foundation and to the National Science Foundation for support of this work.

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Ethylene and Acetylene Complexes of the Silver Atom

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Recently reported low-temperature matrix-isolation ESR studies of the mono- and diacetylene and ethylene complexes of copper and silver atoms have led to the unexpected conclusion that the electronic ground states of the symmetric complexes, where these have been isolated, correlate with the metal atom being in an excited $5p^1(^2P)$ rather than in the ground $5s^1(^2S)$ state.[1,2] In order to quantitatively characterize the geometries of these interesting complexes and gain insight into their electronic structure, we have carried out ab initio self-consistent-field (SCF) calculations on $Ag(C_2H_4)_{1,2}$ and $Ag(C_2H_2)_{1,2}$ using a relativistic effective core potential (RECP)[3,4] for the silver atom and gradient optimization techniques[5] for the geometries.

Restricted open- or closed-shell SCF calculations were carried out on all the systems studied here using the $[3^s2^p/2^s]$ contracted basis described by Dunning and Hay[6] for the carbon/hydrogen atoms. The calculated optimum geometries for C_2H_4 and C_2H_2 in this basis are very close to their respective experimental values, as can be seen from Table I where the optimized geometries are described. For the silver atom the $[3^s2^p2^d]$ valence basis and RECP were taken from previous studies of Ag atom clusters.[3,4]

For the diligand complexes only the symmetric D_{2h} geometry was investigated, where the ligands adopt an eclipsed parallel conformation, one on each side of the silver atom. If the plane containing the Ag and four carbon atoms is defined as XY with Y parallel to, and X bisecting, the C–C bonds, then the four electronic states arising out of the limiting silver atom ^2S and ^2P

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0002-7863/83/1505-6980$01.50/0

Table I. Optimized Geometry Results

	C_2H_4	AgC_2H_4	$Ag(C_2H_4)_2$	C_2H_2	AgC_2H_2	$Ag(C_2H_2)_2$
R_{C-C}, Å	1.334 (1.339)[a]	1.459	1.390	1.202 (1.203)[a]	1.298	1.230
R_{C-H}, Å	1.074 (1.086)[a]	1.078	1.076	1.054 (1.06)[a]	1.086	1.055
∠HCH	116.4 (117.5)[a]	115.7°	116.1°			
bend angle[b]	0°	24.8°	12.2°	0°	37.5°	14.6°
R_{Ag-C}, Å		2.319	2.394		2.278	2.496
state	$^1A_{1g}$	$^2B_1$	$^2B_{2u}$	$^1A_{1g}$	$^2B_1$	$^2B_{2u}$
total energy, au	−78.01180	−116.88646	−194.91191	−76.79885	−115.67634	−192.46757
E_B, eV[c]		1.26	1.63		1.34	1.13
E_R, eV[d]		0.86	2.19		0.99	1.72
spin population						
Ag		0.190	0.336		0.138	0.517
C		0.396	0.166		0.388	0.117
H		0.005	0.000		0.043	0.004
gross population						
Ag		10.540	10.724		10.498	10.830
C	6.361	6.611	6.505	6.264	6.461	6.325
H	0.819	0.809	0.781	0.736	0.788	0.716
δ, eV		1.66	1.63		1.60	~0
β, eV		−2.56	−1.63		−3.33	−0.90

[a] Experimental results in parenthesis from: Hertzberg, G. "Electronic Spectra of Polyatomic Molecules": Van Nostrand: Princeton, NJ, 1966. [b] Angle between CH_2 plane or C–H bond with the C–C axis. [c] Binding energy relative to $Ag(^2P)$ + ground-state ligand(s). [d] Energy of the repulsive $5s^1$ state ($^2A_1$ or $^2A_{1g}$) relative to $Ag(^2S)$ + ground-state ligand(s).

states and the ground-state ligands are $^2A_{1g}$ ($5s^1$), $^2B_{1u}(5p_x{}^1)$, $^2B_{2u}(5p_y{}^1)$, and $^2B_{3u}(5p_z{}^1)$. For both ethylene and acetylene diligand complexes, the $^2B_{2u}$ state was found to be lowest in energy among the $5p^1$ states and bound with respect to its $Ag(^2P)$ + 2 ligand ($^1A_{1g}$) dissociation limit. Analogously, the $^2B_1(5p_y{}^1)$ state was found to be lowest lying in the C_{2v} π-type monoligand complexes, using the same coordinate system. The calculated equilibrium geometries and dissociation energies (E_B) for the complexes in their $5p_y{}^1$ states are tabulated in Table I, as well as the respective spin and gross Mulliken atom populations at those geometries. For all these systems the $5s^1$ state ($^2A_{1g}$ or $^2A_1$) is repulsive with the unpaired spin population residing almost completely in the Ag 5s orbital.

The binding energies, equilibrium geometries, and populations of the $5p_y{}^1$ states generally present an internally consistent picture of the electronic structure of these systems. Thus the diethylene complex is more stable (larger E_B) with a shorter equilibrium Ag–C bond length (R_{Ag-C}) than the diacetylene complex. Both diligand (ML_2) complexes show only relatively moderate changes in the ligand geometries (bond lengths and angles) compared to the free ligands. The differences in E_B and R_{Ag-C} between the corresponding monoligand (ML) complexes are much smaller, and the trends even go in the direction opposite to that found in the diligand complexes. Compared to the ML_2 complexes the monoligand systems have smaller E_B, shorter R_{Ag-C}, and much larger ligand geometry changes. In addition, the ML complexes show larger Ag → ligand (M → L) charge transfer, which probably accounts for their shorter R_{Ag-C} values (electrostatic interaction) and larger ligand geometry changes. The spin population distribution calculated for the $Ag(C_2H_4)_2$ complex (Table I) is in excellent agreement with Kasai's analysis of the ESR spectrum in low-temperature matrix isolation (~$^1/_3$ electron in Ag $5p_y$ and ~$^2/_3$ on the ethylenes).[2]

As pointed out by Kasai,[1,2] for $Ag(C_2H_4)_2$ the $^2B_{2u}$ and $^2B_1(5p_y{}^1)$ states are undoubtedly stabilized by the interaction between the metal $5p_y$ atomic orbital and the ligand $\pi_x{}^*$ molecular orbital(s) (MOs). If the interactions in the ML_2 and ML complexes are treated effectively as single M–L interaction Hückel systems (without overlap), then the two Hückel parameters β (the off-diagonal M-L matrix element) and δ (the diagonal energy difference between the Ag $5p_y$ and the more stable ligand $\pi_x{}^*$ level) can be obtained from the calculated binding energy and spin populations (as the squares of the Hückel MO coefficients) for each of the systems studied here. The resulting fitted δ and β values are also tabulated in Table I.

Since the repulsive $5s^1$ states have their spin populations localized almost completely on the metal atom the ligands are expected to be only minimally changed from their free-ligand geometries. Therefore, for comparison with the corresponding geometry-optimized $5p_y{}^1$ states the $5s^1$ states have been calculated using the free-ligand geometry at the equilibrium R_{Ag-C} bond distance from the appropriate $5p_y{}^1$ state. The resulting repulsive energy (E_R), relative to dissociation [$Ag(^2S)$ + ground state ligand(s)], is found in Table I. Analogous calculations of the $5s^1$ states at the equilibrium ligand geometries gave consistently higher energies in proportion to the degree of difference between the complexed- and free-ligand geometries. Since in these calculations the free silver atom $^2S \rightarrow {}^2P$ excitation energy is calculated to be 3.11 eV it is clear from the tabulated values of E_B and E_R that only for the $Ag(C_2H_4)_2$ complex does the $5s^1$ curve cross the $5p_y{}^1$ curve at larger Ag–C bond distances than the equilibrium R_{Ag-C} value. A rough estimate places this crossing at $R_{Ag-C} \approx 2.55$ Å with a barrier height of ~1200 cm^{-1}, allowing the complex in the $5p_y{}^1$ state to be trapped at very low temperatures. This result parallels Kasai's finding that although all the four possible complexes studied here were attempted only the diethylene complex was observed in the symmetric geometry.

We can now try to correlate the observed electronic structure trends in the bound complexes with possible orbital interactions. The fitted Hückel δ and β values show that the trends in E_B and spin populations between $Ag(C_2H_4)_2$ and AgC_2H_4 can be explained as arising mainly from the different number of M–L interactions in these two cases. For a fixed β/δ ratio, E_B for ML_2 is predicted to be $2^{1/2}$ times E_B for ML, and this ratio is found to be 1.29 for L = ethylene. The different β values found for the two complexes for an almost constant δ value show the correct R_{Ag-C} dependence. Thus, the net Ag–C_2H_4 interaction seems to be about the same in the mono- and diethylene complexes.

The same clearly cannot be said for the $Ag(C_2H_2)_2$–AgC_2H_2 pair. The relative instability and large equilibrium R_{Ag-C} value for $Ag(C_2H_2)_2$ compared to both the diethylene and monoacetylene complexes is an outstanding feature in these results and can possibly be attributed to a repulsive (four electrons in two MOs) interaction between the out-of-plane Ag $4d_{xz}$ and acetylene π_z orbitals. This interaction is essentially absent in the diethylene complex where the carbon $2p_z$ orbitals are tied up in the C–H bonds, and it is suppressed in the monoacetylene complex by the involvement of the Ag $5p_z$ orbital which will stabilize the ligand π_z orbital.

As was noted before, the ability to trap such "excited state" ($5p_y{}^1$) complexes will probably depend on the crossing of the bound $5p_y{}^1$ and repulsive $5s^1$ states with decreasing M–L bond distance. Such a curve crossing will, in turn, depend on the relative stability (E_B) of the $5p_y{}^1$ state and repulsiveness (E_R) of the $5s^1$ state. The more repulsive the $5s^1$ state the greater the chance of such a curve crossing. The monoligand complexes in Table I show uniformly smaller E_R values than their diligand counterparts. This can be attributed to the involvement of the $5p_x$ orbital in the monoligand geometry, which, through hybridization, can moderate the repulsiveness of the 5s orbital in its interaction with the occupied π_x MO of the ligand. On the other hand, the stability of the $5p_y{}^1$ state will strongly depend on the Ag $5p_y$–ligand $\pi_x{}^*$ interaction, which should increase as δ decreases. Analogously, the repulsiveness of the $5s^1$ state will increase as the Ag 5s–ligand π_x energy gap decreases. Thus, for example substitution of Ag by Cu, which has slightly more stable $(n + 1)$s and $(n + 1)$p atomic orbitals,[7] should decrease the $(n + 1)\mathrm{s}{-}\pi_x$ energy differences and enhance the possibility of isolating the $(n + 1)\mathrm{p}_y{}^1$ complex. Substitution of the ligand hydrogen atoms with electron-releasing groups such as alkyl (steric effects aside) should have a similar effect. Substituting Cu for Ag will also give a diacetylene complex with a smaller $n\mathrm{d}_{xz}{-}\pi_z$ repulsive interaction because of the 60% smaller radius of the Cu 3d atomic orbital.[8] For all these complexes, π_x is expected to be stabilized by a reduction in interaction with the metal nd atomic orbital. In fact, Kasai has reported[1] that copper atoms form both ML_2 and ML symmetric complexes with ethylene and acetylene.

Finally, it should be noted that the set of low-lying electronic states described here for the silver–ligand systems is very similar to that found in the rare gas halide and oxide electronic transition lasers which give rise to the familiar "bound–free" laser emission process.[9,10]

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syn-1,6:8,13-Diimino[14]annulene

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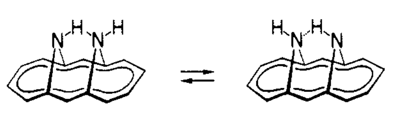
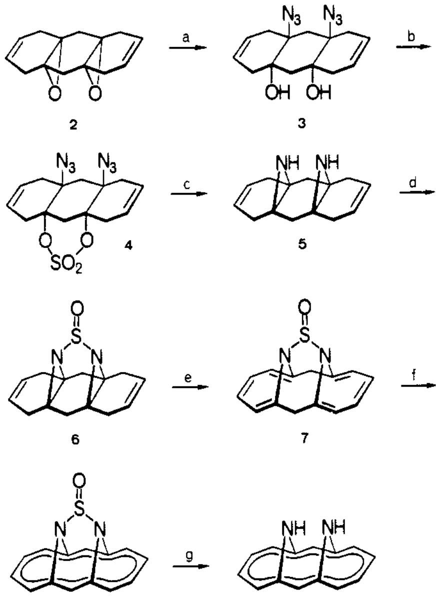
The heretofore elusive *syn*-1,6:8,13-diimino[14]annulene (**1**)[1] features two closely spaced NH groups that are anticipated to have the hydrogens in the exo,endo position [**1a**/**1b**] due to sterically promoted hydrogen bonding. One of the most intriguing aspects of **1** is the possible occurrence of two rather unprecedented degenerate dynamic processes involving the proximate NH groups: (1) a "windshield wiper" flip of the NH protons, tantamount to a tandem configurational inversion of the two nitrogen atoms [**1a** ⇄ **1b**] and (2) an inversion of the two NH bridges through the plane of the [14]annulene ring. While the former process should be detectable by NMR spectroscopy, the latter one might be amenable to examination using chirality of an appropriately substituted 1,6:8,13-diimino[14]annulene as a probe.[2]



1a 1b

After previous unsuccessful approaches toward its synthesis, **1** has now been prepared following a hexahydroanthracene route (Scheme I).

Scheme I



[a] NaN_3 (5 equiv), $MgCl_2{\cdot}6H_2O$, MeOH, reflux, 72 h (64%). [b] Oleum (65% SO_3) (4 equiv), Et_2O, −45 °C, then stirring at room temperature, 12 h (56%). [c] $LiAlH_4$ (2.2 equiv), THF, −25 °C, then stirring at 0 °C, 12 h (75%). [d] $SOCl_2$, Et_3N (2 equiv), Et_2O, 0 °C, then room temperature, 12 h (65%). [e] Br_2 (2 equiv), CH_2Cl_2, −78 °C; DBN (6 equiv), THF, −10 °C, 2 h, then room temperature, 24 h (35% from **6**). [f] DDQ (1.1 equiv), benzene, reflux, 2 h (75%). [g] HOAc/1 N HCl (1:1), 80 °C, 30 min (65%).

1,4,5,8,9,10-Hexahydroanthracene,[3] when epoxidized with 40% peracetic acid, regioselectively afforded **2** and its anti isomer as a 6:4 mixture (95%) from which **2** (mp 187–189 °C, dec; 45%) was separated by chromatography on silica gel (dichloromethane/ethyl acetate).[4] Interestingly, **2** on treatment with sodium azide in methanol in the presence of magnesium chloride[5] experienced regioselective opening of the two epoxide rings to give as the only product the diazido diol **3** (mp 201–202 °C dec; 64%),[6] whereas the anti isomer reacted only sluggishly under these conditions yielding ill-defined products. This reactivity pattern obviated the tedious separation of the *syn-anti*-bis(epoxide) mixture. At the stage of **3**, the synthesis of **1** was stymied for quite some time, since this intermediate defied all attempts at acylation to convert its hydroxy functions into leaving groups. Even such powerful acylating agents as triflic anhydride or sulfuryl chloride (entropy-assisted formation of the cyclic sulfate **4**) left **3** virtually unaffected.

Finally, the desperate experiment of reacting **3** with oleum (ca. 65% SO_3)[7] in ether met with success in that it afforded **4** as the

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(1) Bridged [14]annulenes with an anthracene perimeter are already known in great structural variety. For reviews see: (a) Vogel, E. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1968**, *12*, 215–251; (b) *Pure Appl. Chem.* **1969**, *20*, 237–262; (c) *Ibid.* **1971**, *28*, 355–377; (d) *Isr. J. Chem.* **1980**, *20*, 215–224; (e) *Pure Appl. Chem.* **1982**, *54*, 1015–1039. (f) Nozaki, H., Ed. "Current Trends in Organic Synthesis": Pergamon Press: Oxford and New York, 1983; pp 379–400.

(2) An inversion of this type has recently been detected in the *syn*-1,6:8,13-diepoxy[14]annulene system by employment of optically active 2,9-dibromo-*syn*-1,6:8,13-diepoxy[14]annulene, private communication by Prof. K. Schlögl, University of Vienna, Austria.

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