ration in the mixed valence salt IV. For TTF$^+$, however, with its lower reduction potential than TSeF$^+$,[11] an electron transfer reaction corresponding to eq 1 is not thermodynamically as favorable (Table I). Neutral TTF would not be present in this solution and therefore the stoichiometric 1:1 salt III is formed. Likewise, treatment of the radical cations with Cl$^-$, which has a lower oxidation potential[14] than Br$^-$, leads to the formation of the 1:1 insulating TSeFCl salt V.[15] However, we have found that the mixed valence chloride salts can be prepared from these donors when *both* neutral and cation species are present through partial electrochemical oxidation.[6,16]

These results indicate that the redox chemistry of acceptor anions must be considered when using these species as synthetic reagents in conjunction with donor ion radicals. For example, the multiple TTF-iodide stoichiometries[5,7,9a] that have been found and the inability to form a simple 1:1 iodide salt[16] are undoubtedly related to the multiple, low energy redox states[14,17] (I^-, I_3^-, I_2) for the anions typically used. More importantly, it appears that electrochemical techniques offer unique synthetic and mechanistic tools to this new area of chemistry. As shown here, formation of a single specific product can be achieved via synthetic control over the stoichiometry of the reactants by appropriate choice of specific donor–halide acceptor pairs. In the absence of complicating factors (e.g., nonequilibrium conditions, large differences in solubility products, etc.) the relative redox potentials of organic donor and halide may be useful in predicting product stoichiometries. Furthermore, the electrochemical technique has also enabled us to prepare product mixtures which contain *both* the 1:1 and the structurally[6] dissimilar mixed valence salt.[18] Thus, the tendency to form particular solid-state stacking structures as a function of donor molecular properties can now be evaluated quantitatively.

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Bidentate and Monodentate Bonding Modes of the 1,3-Diaryltriazenido Ligand in Ruthenium(II) and Platinum(II) Complexes

Sir:

The ligands allyl ($R_2CC(R')CR_2$), carboxylato ($OC(R')O$), amidino ($RNC(R')NR$), and triazenido ($RNNNR$), although isoelectronic, offer a variety of reaction chemistries and bonding arrangements in the presence of transition metals. Each is potentially either a one- or a three-electron donor to the metal. Of this series the latter two, namely amidino and triazenido, appear to have been studied least. Recent interest in these two ligands is apparent.[1-11] A key to understanding the reaction chemistry is the mode of attachment of the ligand to the metal. On the basis of spectroscopic data, structures involving these ligands in monodentate, bidentate, and bridging bonding modes have been proposed. Yet interpretation of these spectroscopic data is not without controversy.[1,2] Surprisingly few x-ray results are available for these metal–ligand systems. In $[Cu(dpt)]_2$ (dpt = 1,3-diphenyltriazenido),[12] $[Ni(dpt)_2]_2$,[13] $[Pd(allyl)(dtt)]_2$ (dtt = 1,3-di-*p*-tolyltriazenido),[3] $[Cu(dmt)]_4$ (dmt = 1,3-dimethyltriazenido),[14] $RhCuCl(CO)(PPh_3)_2(dmt)$,[8] $[Mo(dpb)_2]_2$ (dpb = *N,N'*-diphenylbenzamidinato),[10] and $Re_2(dpb)_2Cl_4$,[11] the ligand bridges metal centers. The bidentate bonding mode for triazenides has been confirmed structurally in $Co(dpt)_3 \cdot C_6H_5CH_3$[15] with the two terminal N atoms of each ligand bonded to Co. Although the monodentate mode of bonding for triazenides has been proposed[1,4,16] and disputed[2] on the basis of ir and NMR data, no structural example had previously been found. Here we report on the x-ray crystal structures of two triazenido complexes, $RuH(CO)(PPh_3)_2(dtt)$ and *cis*-$Pt(PPh_3)_2(dpt)_2$. The former shows the bidentate mode of bonding while the latter provides the first example of the monodentate mode of bonding.

Orange crystals of $RuH(CO)(PPh_3)_2(dtt)$ were obtained by recrystallization of material kindly provided by Dr. S. D. Robinson. The space group is $P\bar{1}$ with a = 14.074 (2), b = 15.264 (3), c = 12.195 (2) Å, α = 109.78 (1), β = 111.74

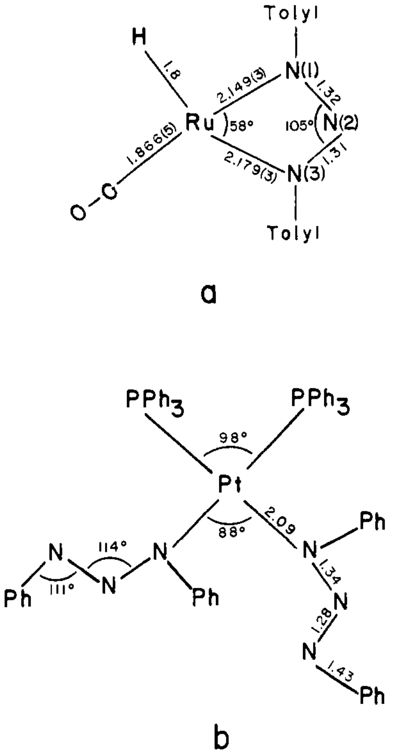

Figure 1. A diagram of (a) the $RuH(CO)(PPh_3)_2(dtt)$ and (b) the *cis*-$Pt(PPh_3)_2(dpt)_2$ complexes showing relevant bond distances and angles (the estimated standard deviations are 0.01 Å and 0.5° unless otherwise shown). Average values are given for the two crystallographically independent dpt ligands in the Pt complex. The phosphines in the Ru complex have been omitted for clarity.

(1), $\gamma = 65.03\ (2)°$, and $V = 2154$ Å^3; $Z = 2$, $\rho_{calcd} = 1.35$, and $\rho_{obsd} = 1.34$ g cm^{-3}. Intensity data were collected on a Picker FACS-I computer-controlled diffractometer using Ni-filtered Cu Kα radiation and operating in the θ–2θ scan mode. The crystal structure was solved and refined by standard procedures. For 5847 independent data with $F_o^2 > 3\sigma(F_o^2)$ the R index is 0.038.

As illustrated in Figure 1, the bidentate dtt ligand bonds symmetrically to the Ru atom. The N(1)–N(2)–N(3) angle of 105.2 (3)° and the average N–N bond length of 1.314 (4) Å agree very well with those reported for the $Co(dpt)_3$ complex.[15] The Ru–N(3) distance of 2.179 (3) Å is longer than the Ru–N(1) distance of 2.149 (3) Å owing perhaps to the greater trans influence of the hydrido compared with the carbonyl ligand. The average N to phenyl C distance of 1.415 Å is typical.[17] The atoms of the ditolyltriazenido group are nearly coplanar; this situation contrasts with the $Co(dpt)_3$ complex in which the two phenyl groups within each dpt ligand are twisted about 20° with respect to one another,[15] presumably a result of placing three dpt ligands in such close proximity.

The $Pt(PPh_3)_2(dpt)_2$ complex was prepared by literature methods.[1] Red-orange crystals of what turned out to be the cis isomer were deposited from the mother liquor (benzene solution) to which methanol had been added. The crystals of *cis*-$Pt(PPh_3)_2(dpt)_2{\cdot}C_6H_6$ belong to space group $P2_1/n$ with $a = 10.797\ (1)$, $b = 23.048\ (3)$, $c = 22.034\ (3)$ Å, $\beta = 91.08\ (1)°$, and $V = 5482$ Å^3; $Z = 4$, $\rho_{calcd} = 1.44$, and $\rho_{obsd} = 1.43$ g cm^{-3}. Intensity data were collected under the same experimental conditions as for the ruthenium complex. The structure was again solved and refined by standard methods. For 7923 independent data having $F_o^2 > 3\sigma(F_o^2)$ the R index is 0.045.

The relevant bond distances and angles for the *cis*-$Pt(PPh_3)_2(dpt)_2$ molecule are given in Figure 1. The most important feature of the structure is the monodentate bonding of both of the dpt ligands to the Pt. The two P atoms and the two Pt-bonded N atoms define the square-planar geometry of the complex. The two N atoms of each of the dpt ligands that are not bonded to the metal atom are 3.0 Å from the Pt. Whereas the two N–N bond lengths are virtually equal in the bidentate Ru complex, owing to the delocalization of the π-electrons in the triazenido moiety, there is a significant difference in the monodentate Pt complex. In the canonical structure, the N–N bond adjacent to the Pt is a single bond, and the bond away from the metal is a double bond; whereas the former bond is indeed longer (1.336 (6) Å) than the latter (1.278 (6) Å) for both dpt ligands, significant π-delocalization is evident when a comparison is made with typical N–N single- and double-bond lengths of 1.44 and 1.24 Å, respectively.[17] The average N–N–N angle of 113.8 (4)° is considerably greater than the 105.2 (3)° found in the bidentate Ru complex; the larger angle compares favorably with the 116° value found in the bridged triazenido complexes of Cu(I)[12] and Ni(II).[13] This fact emphasizes the strained nature of the $\overline{\text{Ru–N(1)–N(2)–N}}(3)$-four membered ring. As for the Ru complex, all of the atoms in one of the dpt ligands are virtually coplanar. In the second dpt ligand, however, one of the phenyl rings is twisted 43.2° with respect to the other phenyl ring. Thus, the energy differences between the two conformations must be relatively small.

Because not all the bonding capabilities of the triazenido ligand are utilized in this Pt complex, the reaction chemistry of the molecule toward coordinatively unsaturated transition metal systems is being investigated. It appears that the triazenido ligand, which has now been demonstrated to enter into varied bonding modes with one or more transition metals, has a rich chemistry that to date has been only slightly explored.

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