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Molecular Orbital Theory of Organometallic Compounds. XIV.[1] The Electronic Structures of Metal-Allyl Complexes

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The electronic structures of a series of bis-π-allyl metals (A_2M, M = Ni, Pd, Pt) and π-allyl metal chloride dimers ($(AMCL)_2$, M = Ni, Pd, Pt) have been investigated by the SCCMO method as outlined in previous papers in the series. The metal-carbon overlap populations lie in the sequence $Ni \sim Pd < Pt$ for the bis π-allyl metals and in the sequence $Ni < Pd < Pt$ for the halogen bridged dimers. The overlap populations for the halogen bridged dimers are always greater than for the corresponding members of the first series, again in agreement with the observed stability sequence for Ni and Pd compounds. Our calculations predict the existence of a stable series $(APtX)_2$, X = Halogen. The π-allyl ligand is primarily an electron-donating ligand and, in the presence of electron-attracting groups being attached to the central metal, functions almost exclusively in this mode.

Introduction

Complexes involving the allyl radical acting as a three-electron ligand with various transition metals have been known for well over a decade,[2] the majority being restricted to metals of the first transition series with the exception of Pd and Pt. In this paper we describe the electronic structures of pure allyl complexes of formula $M(\pi\text{-allyl})_2$, M = Ni, Pd, Pt, bridged complexes $(M(\pi\text{-allyl})Cl)_2$ M = Ni, Pd, Pt by application of the self-consistent charge and configuration molecular orbital method (SCCCMO). In the previous papers in this series[1] we found the above method to be successful in calculating a range of ground state quantities such as orbital energies and overlap populations and relating these to observed properties such as ionization potentials, photoelectron spectra, vibrational force constants and frequencies. These correlations were obtained without any variation in a given set of wavefunctions for a given metal and ligand. In the present work we hoped to provide a rationalization of the known data for a comparable series of metal allyl complexes and, in part, to predict properties of some unknown or imperfectly characterized compounds.

Although many papers have discussed various aspects of metal allyl complexes, e.g. conformational problems such as σ-π complex equilibria there is a dearth of reliable physical data on a strictly comparable series (e.g. photoelectron spectra, bond energies, force constants) — indeed this remark is true of much of organometallic chemistry when one considers the thousands of preparative papers now published. In a comprehensive review,[3] Wilke remarked that « In a given group of the periodic system the stabilities of the allylmetal compounds increase with atomic number of the metal », for example $Ni < Pd < Pt$; $Cr < Mo < W$ but surprisingly, however, the yields decrease within each triad in the order of increasing stability. Accordingly, we wished to ascertain whether the SCCCMO method could explain or rationalize the above order and in so doing provide an insight into the type of bonding in these complexes. We consider first the simple sandwich bis allyl metal compounds A_2M(A=π-allyl, M=Ni, Pd, Pt) then bridged Metal allyl halogen compounds $(AMX)_2$ (A=π-allyl, X=Cl, M=Ni Pd and Pt) which certainly in the case of palladium are known to be much more stable than the corresponding sandwich compounds.

Method of Calculation

Bis π-allyl metals, A_2M (M = Ni, Pd, Pt). The SCCCMO method has been fully described by us previously. Richardson functions[4] were used for the nickel, 3d 4s and 4p atomic orbitals. Basch and Gray functions were employed for the Pd and Pt cases assuming an initial zero charge on the metal. VOIP values for Pd and Pt were derived from Moores tables[5] in a similar manner to that of Basch and Viste[6] and may be obtained from the authors by those interested. Slater functions[7] were used for the carbon, 2s and 2p atomic orbitals.

The π-orbitals of the allyl group were obtained by application of the SCCCMO method to the free ligand assuming a value for the coulomb term of the carbon 2p orbital (H_{cc}) of 8.358 e.v. estimated from the available VOIP values allowing for hybridisation. This method gave a calculated ionization potential of 8.09 e.v. for the allyl radical in excellent agreement with an experimental value of 8.16 e.v. (8). The σ-orbitals were neglected.

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(5) C.E. Moore, « Atomic Energy Levels » Circular 467, N.B.S. Washington D.C., (1952, 1958).

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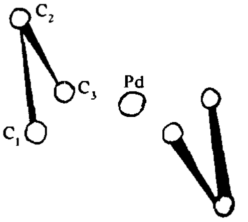
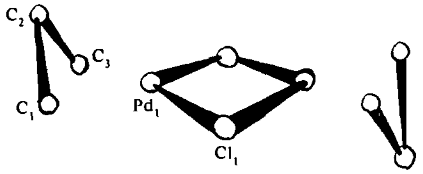
The geometry of the complex is assumed to be the same as that obtained from X-ray studies of bis π-methallyl nickel[9] which possess C_{2h} symmetry with the metal atom occupying the centre of symmetry. The interatomic distance for bis π-allyl nickel were taken directly form reference 9. No data is available for the Pd and Pt complexes but by analogy with published data for the bridged $(PdallylCl)_2$[10] and other palladium complexes ([11]) an increase in d(M–C) from 1.98 Å to 2.21 Å in going from Ni to Pd was assumed. Comparison between analogous Pt and Pd complexes led us to take the (Pt–C) distance as the same as the (Pd–C). The symmetry classification for the interactions is this model was first given by Green ([2]) and no further details are necessary. Group overlap integrals were calculated by standard computer programmes.



$(allyl)_2Pd$



$(allylPdCl)_2$

Figure 1.

Bridged π-allyl metals $(AMCl)_2$, *M = Ni, Pd, Pt.* Detailed structural results are available for the Pd complex ([10]). The same geometry was asumed for the Ni and Pt complexes and again a contraction of 0.14 Å for the Ni–C distance and identical Pt–C distance compared to the published Pd–C distance were assumed. The total symmetry is still C_{2h} but the metal atom no longer occupies the centre of symmetry (see Figure 1); nevertheless, the idealized symmetry classification for a half of the molecule given by Vrieze and coworkers ([12]) applies to our calculations also. The same functions were used as above and Clementi functions ([13]) were used for the chlorine s and p orbitals. As the SCCCMO method is only selfconsistent with respect to charge on the metal atom the charge on the bridging chlorine atoms was estimated from Pauling's relationship between bond ionic character and electronegativity which gave a charge on the chlorine of –0.2 (taking$\chi_{Pd}=2.2\chi_{Cl}=3.0$) which is close to estimates made for this quantity in the $Mn(CO)_5X$ series (1). Direct interaction between the allyl groups and between the allyl and chlorine atoms was neglected. The remaining application of the SCCCMO method is standard.

Results and Discussion

Energy Levels and Photoelectron Spectra The orbital energies together with calculated vertical ionization potentials (assumed by Koopman's theorem ([14]) to be equal in energy to that of the highest occupied orbital) are given in Table I. Because of the considerable number (20) of occupied orbitals for the bridged $(AMX)_2$ complexes these have been omitted from the Table but can be obtained from the authors on request; moreover, no ionization potentials nor photoelectron spectra have been published for these compounds.

Table I. Orbital Energies of $M(allyl)_2$.

M(allyl) (Energies e.v.)	Orbital Energies (e.v.)		I.P. (calc.)	I.P. (obs.)
Ni	1 A_g	10.829	8.19	—
Total E = 149.222	1 B_u	10.101		
	1 B_g	9.609		
	2 A_g	9.074		
	3 A_g	9.029		
	2 B_g	9.029		
	4 A_g	8.752		
	1 A_u	8.188		
Pd	1 A_g	11.057	8.16	7.85
Total E = 158.235	1 B_u	10.537		
	1 B_g	10.107		
	2 A_g	10.060		
	3 A_g	10.009		
	2 B_g	10.009		
	4 A_g	9.181		
	1 A_u	8.159		
Pt	1 A_g	11.158	8.31	—
Total E = 153.630	1 B_u	10.241		
	1 B_g	10.102		
	2 A_g	9.390		
	3 A_g	9.301		
	2 B_g	9.301		
	4 A_g	9.014		
	1 A_u	8.308		

In the case of A_2M (M = Ni, Pd and Pt), whilst this work was in progress we learnt that the P. E. spectrum of the sandwich palladium and nickel compounds have been measured (15,20) and are given in Table II. Again, as in our studies of metal carbonyl complexes, the overall agreement is encouraging and lends confidence to the results of our calculations for

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Table II. Photoelectron Spectra of $Ni(Allyl)_2$[15] and $Pd(allyl)_2$[20].

Ni(allyl)₂ Vertical I.P.	Intensity	Probable Assignment	Calcd. Levels	Pd(allyl)₂ Vertical I.P.	Intensity	Probable Assignment	calcd. Levels
7.85	2	« d »	8.19	7.59	2	« d »	8.16
			8.72				9.18
8.17	2	»	9.03	8.74	1	»	10.01
			9.03				10.01
8.59	1	»	9.07	9.22	1	»	10.06
9.48	1	« allyl π »	9.61	9.52	1	»	
10.44	1	»	10.10	9.73	1	« allyl π »	10.11
11.56	1	»	10.83	10.43	1	»	10.54
12.75	4	« allyl σ »	—	11.56	1	»	11.06
14.20	2	»	—	12.83	4	« allyl σ »	—
15.73	2	»	—	14.13	2	»	—
17.67				15.61	2	»	—
				(17.66)			

Table III. Net Charges, Charge Transfer and Overlap Populations in Metal Allyl Complexes.

Complex	(M—C) pop	Q_{allyl}	Q_M	Charge Transfer 1Ag 1Bu	Bg Au	2Ag 2Bu
A_2Ni	0.1752	0.072	+0.028	—0.279	+0.228	+0.028
A_2Pd	0.1779	0.132	—0.085	—0.230	+0.158	+0.030
A_2Pt	0.2510	0.314	—0.337	—0.430	+0.188	+0.052
				$(1B_1)$	(A_2)	$(2B_1)$
$(ANiCl)_2$	0.1992	0.585	—0.034	—0.318	—0.300	+0.032
$(APdCl)_2$	0.2171	0.712	—0.112	—0.278	—0.472	+0.048
$(APtCl)_2$	0.2766	0.599	—0.319	—0.250	—0.420	+0.072

at least this molecule. Apart from purely symmetry classifications of the interactions in $(\pi\text{-allyl})_2M$ by Green ([2]) and a qualitative account ([16]) which largely discounted back–bonding by the π-allyl group, Hillier ([17]) has given a semi–quantitative discussion of bis-π-allyl palladium which also took into account the framework of the allyl radicals. Where comparison is possible our more empirical approach gives better agreement with the observed photoelectron spectrum than the above calculation ([17]) probably due to the lower coulomb terms of the carbon atomic orbitals quoted by Hillier. Finally, an ab initio calculation ([18]), together with correction ([19]) of bis-π-allyl nickel taking into account all valence electrons predicted an I.P. of 9.61 e.v. which compares with our value of 8.19 e.v.

Metal-C overlap populations and charge distributions. Mulliken overlap populations for the M–C-(allyl) bond (treated as a 3-centre interaction with the metal M) together with the net charges on the allyl group and meal atom are given in Table III.

For the A_2M series, a progressive increase occurs in the M–C overlap population in the sequence $Ni \sim Pd < Pt$ which is in reasonable accord with Wilke's general observation that the stability of the bis-π-allyl compounds increase down the above triad. The charge distributions indicate that certainly for the nickel and palladium complexes the metal is essentially uncharged and the complexes are largely covalent in character in contrast to the ab initio calculations on A_2Ni which suggested a rather ionic bond. Moreover, in terms of the generally accepted classification of covalent and ionic bond types (for example, as categorized in a recent review by Nyholm[21]), the metal-allyl complexes possess reasonably covalent bonds as evidenced, for example, by their volatility.

Comparison of the bis π-allyl metals with the halogen bridged compounds $(AMCl)_2$ reveals a marked change in stability. The overlap populations given in Table III for this latter group are much greater than for the A_2M series, most especially in the case of the nickel compounds. Evidently coordination of a halogen in place of an allyl group greatly enhances its electron donating ability and, at the same time, removes excess negative charge from the metal atom. Again these trends are in excellent agreement with the general properties of the bridged allyl metal complexes since these are much more stable than the corresponding A_2M compounds. For example bis π-allylnickel is pyrophoric and decomposes at 0°C,[22] whereas, the π-allyl nickel halides can be prepared without undue difficulty and undergo bridge cleavage reactions with nucleophiles such as triphenylphosphine with the formation of allyl $NiClPPh_3$ type compounds with retention of the nickel-allyl bond. Similarly, the π-allyl palladium halides are very stable and can be easily handled in air at room temperature although less stable in solution. It follows also from Table III that because the (M–C) overlap populations (column 2) are greater for $(APtCl)_2$ than for the corresponding Pd compounds, we predict the existence of a stable platinium series. To the best of our knowledge no simple platinium halogen-bridged π-allyl

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complexes have been reported authough Table V of reference 2 records them but this appears to be a typographical error since the reference quoted for this entry refer only to the Pd series. In Table III we give the net charges on the metals calculated for the various ligand-metal molecular orbitals and the principal ligand orbitals from which they are derived. The numbers in columns 5, 6, and 7 give the net charges on the ligand orbitals involved in bonding with the metal atom. Essentially the fifth column denotes charge transfer from the bonding π-orbitals of a free allyl ligand to the metal atom (hence the notation of a negative sign), the sixth column involves the nonbonding empty π-orbital and the seventh column, the antibonding empty π-orbital of the free ligand. It can be seen that in both the sandwich A_2M and dimeric halogen bridged $(AMX)_2$ compounds the bonding π-orbital acts as an electron donor to the metal as expected. However, the non-bonding orbital acts in the sandwich compounds as a definite acceptor orbital whereas in the bridged compounds the powerful electron-attracting halogen atoms cause this orbital to became electron-donating and thereby probably results in the increased stability of these complexes relative to the A_2M series as noted above because the non-bonding orbital appears to be a relatively poor electron-acceptor. Finally the empty antibonding π^* orbital of the allyl group in both types of compounds acts as an electron-acceptor but to a smaller extent than with ligands such as CO or NO. Our results are in some contrast to the previous qualitative discussion of Vrieze *et al.*[12] in which it was concluded that interaction of the non-bonding π allyl orbital and metal d_{yz} orbital led to equal sharing. We find that the bridging halogen causes this interaction to be a definite electron-donating effect and our increased M—C overlap populations support this view and are in accord with experiment. Indeed our theoretical results suggest a rationalization of metal-allyl complex chemistry if one accepts the above fact. For example, complexes of the form A_4M and A_3M would be exnected for metals (M) which have a small requirement for back-donation e.g. Zr. Similarly if CO is bonded to a metal then because of its strong π-acceptor character complexes of the form $AM(CO)_x$ become relatively stable compared to A_2M because in the former compound the π-allyl ligand is not forced to act as a π-electron acceptor in the presence of CO. Indeed our calculations make exactly this point for $(AMX)_2$ compared to A_2M.

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