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A Photoelectron Spectroscopic Study of $[Rh(CO)_2Cl]_2$.

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Summary.

The He(I) and He(II) vapor phase photoelectron spectra of the $[Rh(CO)_2Cl]_2$ dimer have been measured and interpreted with the aid of the results of a non-empirical pseudopotential calculation. The relative He(I)/He(II) band intensity ratios indicate that the spectrum is essentially divided into Rh 4d, Cl 3p and CO σ,π ionization regions. Ionization potential shifts between the free and complexed moieties suggest that there is only a small nett transfer of electron density from Rh to Cl and CO.

Introduction.

The dicarbonylchlororhodium (I) dimer, $[Rh(CO)_2Cl]_2$, is used widely as a reagent in organic and organometallic synthesis. X-ray diffraction data [1] for $[Rh(CO)_2Cl]_2$ in the solid state has shown that the molecule consists of two essentially planar $(OC)_2RhCl_2$ halves which intersect at an angle of 124° along the Cl --- Cl axis. A bent

Rh-Rh bond has been proposed [1] to account for the folding in the structure. An alternative suggestion [2] that the bending is due to packing forces within the crystal seems inconsistent with observations that the bent conformation is retained in solution [3,4].

Whereas there are similar bent structures exhibited by $[Rh(C_2H_4)_2Cl]_2$ [5], $[(COD)RhCl_2Rh\{P(OPh)_3\}_2]$ [6] and $[Rh(CO)(PMe_2Ph)Cl]_2$ [7], the related complexes $[Rh(COD)Cl]_2$ [8] and $[Rh(PPh_3)_2Cl]_2$[9] have coplanar structures.

In several theoretical studies the nature of the Rh-Rh bonding involved in the bent complexes has been investigated. An extended Huckel model [2] found that there was no direct interaction of metal orbitals which would favor a bent rather than a planar structure. A SCF-Xα-SW calculation on $[Rh(CO)_2Cl]_2$ [10] concluded that the bending is enhanced principally by the occupation of orbitals associated with the Rh_2Cl_2 system, which are mainly Cl 3p, rather than Rh 4d, in character. A recent non-empirical pseudopotential calculation [11] showed that the bent C_{2v} form was preferred by 4.1 kcal mol^{-1} over the planar D_{2h} geometry, and that no Rh-Rh bond existed in either structure.

The need for experimental evidence relating to these ideas together with our general interest in chloro-bridged metal complexes, has prompted an investigation of the UV photoelectron (PE) spectra of $[Rh(CO)_2Cl]_2$. The presence of Cl atoms makes this a model compound for a comparative He(I)/He(II) study because the bands associated with Cl 3p character should not only fall in an ionization potential (IP) region between Rh 4d and CO σ,π bands, but should also be greatly reduced in relative intensity in going from the He(I) to the He(II) ionizing line [12].

Experimental.

The deep red crystalline $[Rh(CO)_2Cl]_2$ was obtained from hydrated rhodium (III) chloride by reduction with CO [13]. Samples were placed in a resistively heated glass inlet system fitted to a double-chamber photoelectron spectrometer [14]. Heating to about 40°C gave sufficient vapor pressure for spectral measurements. Time-averaged spectra of 512 points were obtained over 2 hr periods, the He(I) spectrum at a maximum count rate of 500 s^{-1}, and the He(II) spectrum at 40 s^{-1}. The He(II) spectrum was smoothed with a 6 point gaussian function, and the IP scale was obtained by calibration with a butadiene/argon mixture.

Results and Discussion

The He(I) and He(II) PE spectra of $[Rh(CO)_2C\ell]_2$ are shown in figure 1, and the 30 IPs expected below 20 eV are summarized in table 1, where they are compared with the theoretical values obtained from the non-empirical pseudopotential calculation of Serafini et al. [11]. In general terms, the filled molecular orbitals (MOs) can be described as comprising 8 MOs having mainly Rh 4d character, followed by 6 Cℓ 3p-based MOs, with a considerable energy gap to the more stable MOs based on combinations of the CO 2p-based σ and π MOs.

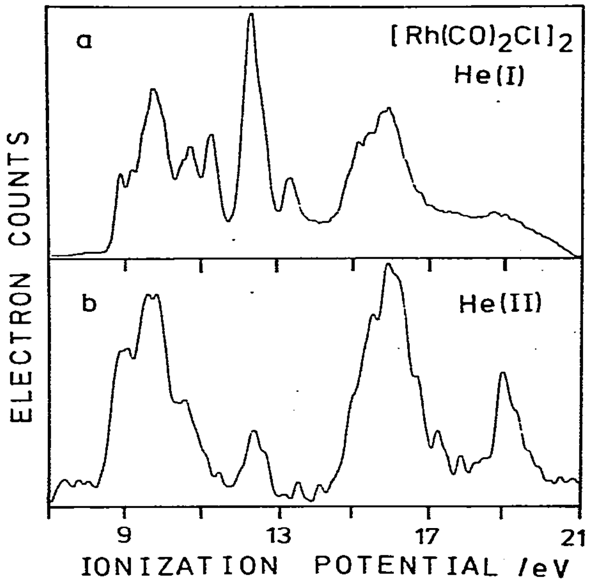

Figure 1. UV photoelectron spectra of $[Rh(CO)_2C\ell]_2$.
(a) is the time averaged He(I) spectrum, and (b) is the time-averaged and smoothed He(II) spectrum.

Table 1. Comparison of Experimental and Calculated Ionization Potentials (in eV) and Molecular Orbital Assignments of $[Rh(CO)_2C\ell]_2$.

IP[a]	Designation	MO[b]	-0.8ε[c]
8.89	Rh	$9b_2$	9.21
9.20	Rh	$9b_1$	9.34
9.50 – 10.0	3Rh + Rh-Cℓ	$11a_1$	9.42
		$10a_1$	9.56
		$8b_1$	10.09
		$7a_2$	10.58
10.5	Rh	$7b_2$	11.01
10.74	Rh-Cℓ	$8b_2$	10.14
11.30	Rh-Cℓ	$9a_1$	10.71
12.0 – 12.6	3Cℓ + Rh-Cℓ	$6a_2$	11.45
		$7b_1$	11.67
		$8a_1$	11.84
		$6b_2$	11.97
13.36	Rh-Cℓ	$7a_1$	12.98
15.16	2 CO,σ	$5a_2,6b_1$	
15.44	2 CO,σ	$5b_2,6a_1$	
15.7 – 16.7	8 CO,π	$5a_1,4a_1,4a_2,$ $3a_2,5b_1,4b_1,$ $4b_2,3b_2$	
18.0 – 20.0	4 CO,σ	$3a_1,2a_2,3b_1,$ $2b_2$	

a. Accuracies vary between ±0.03 and ±0.10 eV.

b. MOs are numbered within the valence shell for C_{2v} symmetry.

c. The uppermost 14 eigenvalues given in reference 11 are scaled appropriately for the double-zeta basis used.

The distribution of bands in the measured spectra correlates very well with the distribution of calculated IPs. The Rh 4d bands fall between 8.89 and 10.74 eV giving a spread of 1.85 eV compared to a value of 1.80 eV obtained from the scaled MO data. The Cℓ 3p bands range from 11.30 to 13.36 eV giving a spread of 2.06 eV which compares favourably with the theoretical value of 2.27 eV. Details of the CO-based bands of the complex were not included in the theoretical paper [11].

A visual comparison of the He(I) and He(II) spectra clearly shows the relatively low intensity expected for the MOs of high Cℓ character in the 11-14 eV region of the He(II) spectrum. The CO-based bands in the 14-17 eV region are effectively the same at both He wavelengths though the 19 eV bands are enhanced in the He(II) spectrum because of the decrease in analyser transmission which affects the low kinetic energy electrons involved in the He(I) case.

The relative He(I)/He(II) intensities in the 9-11 eV Rh 4d band region are of greater interest because they exhibit more subtle differences. The highly localized non-bonding 4d orbitals are expected to show He(II) enhancement relative to the CO-based bands. This occurs for the lowest IP bands at 8.89 and 9.20 eV, which can then be assigned as of localized Rh character. By contrast the relatively intense overlapped band region from 9.5 - 10.5 eV is diminished somewhat under He(II) conditions suggesting that Cℓ character is present and that some of these bands correspond to slightly stabilized Rh-Cℓ bonding orbitals. The two closely overlapped bands with maxima at 10.5 and 10.74 eV change dramatically in relative intensity in going from He(I) to He(II) indicating that the higher IP band has considerable Cℓ character.

The correlation of the 14 uppermost MOs of Serafini et.al.with the suggested IP assignment in table 1 is uniformly good, with the appropriately scaled eigenvalues generally within 0.4 eV of the experimental values. The relative positions of the Rh and Cℓ bands and the spread of Cℓ 3p character indicated by the He(II) intensities agrees with the conclusion of the theoretical study that the structure of $[Rh(CO)_2C\ell]_2$ is dominated by Rh-Cℓ bonding.

The main feature of the CO-based bands is their relationship to the free-molecule IPs which have a $3\sigma < 1\pi < 2\sigma$ pattern. The highest band at 19.0 eV is clearly associated with interaction of the four 2σ MOs of the COs, and it shows a considerable reduction of 0.7 eV from the free-molecule value. The overlapped bands in the 14.5 - 17 eV region are of more interest because they show that the 3σ and 1π MOs originating from the four COs have drawn closer together in the complex. Due to bonding with Rh the 3σ MO has stabilized by an average of 1.3 eV, whereas the 1π MO has destabilized by an average of 0.9 eV. This coalescence of the 3σ and 1π levels is also observed in the PE spectra of binary metal carbonyls [15-17] as well as when CO adsorbs on metal surfaces [18,19].

In the qualitative MO picture of CO [20], the 2σ MO is of mainly C 2s character and is stabilized by $\sigma_s - \sigma_z$ interaction involving the 3σ MO. In the complex the increased 3σ IP matches the decrease in the 2σ IP, and the reduced 2σ - 3σ splitting is consistent with a lengthening of the C-O bond which accompanies Rh-C bonding. The lowered 1π IP is indicative of the same change.

While these effects clearly indicate the presence of strong Rh-CO bonding, the question of whether the interaction utilizes mainly σ or π orbitals, or both, is difficult to answer. Because of their variation with small changes in geometry, the CO PE bands are analogous to the CO bond stretching frequency in acting as a sensitive probe of the bonding effects in carbonyl complexes.

Whereas the calculation by Serafini et.al. [11] indicates a reasonable redistribution of electron density in the complex with local atomic charges of Rh -0.11, Cℓ -0.13 and CO +0.12, a simple analysis based on the PE spectrum suggests that there is a much smaller movement of electron density. A simple quantitative description of an inductive effect on IP is that a gain in local atomic charge Δq can be approximated as $\Delta I/I_o$ where ΔI represents an increase in experimental IP over the neutral fragment IP of I_o [21]. In $[Rh(CO)_2C\ell]_2$ the non-bonding Cℓ IPs occur at 12.3 eV compared to a neutral Cℓ IP (the mean of the π_g and π_u IPs of $C\ell_2$) of 13.0 eV. Hence Δq is $-0.7/13.0 = -0.05$. The CO $3\sigma, 1\pi$ bands have weighted mean IPs of 15.8 and 15.6 eV for the free and complexed states respectively giving a Δq of $-0.2/15.8 = -0.01$ for each CO. The calculation for Rh is more difficult because there is no obvious free atom 4d valence IP. Consequently it is easier to regard the Rh as losing electron density to obtain the balancing charge of +0.07. In comparison to the binary metal carbonyls, where the centre-of-gravity of the CO $3\sigma,1\pi$ bands is around 14.5 eV, representing a larger electron gain by CO, the Cℓ bridging atoms in $[Rh(CO)_2C\ell]_2$ clearly gain electron density from the Rhs at the expense of the CO ligands.

Conclusion.

The $[Rh(CO)_2C\ell]_2$ dimer represents a model system for a comparative study by He(I) and He(II) photoelectron spectroscopy. An analysis of the spectra agrees with the theoretical molecular orbital description of the bent C_{2v} structure of the molecule, that strong Rh-Cℓ interactions occur with the exclusion of any direct Rh-Rh bonding. While Rh-CO bonding slightly weakens the C-O bonds, there is very little electron transfer to the CO ligands, as the bridging chlorines gain most of the small amount of electron density lost by the rhodium atoms.

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References

1. L.F. Dahl, C. Martel and D.L. Wampler, J.Am.Chem.Soc., 83 (1961) 1761.
2. R.H. Summerville and R. Hoffman, J.Am.Chem.Soc., 98 (1976) 7240.
3. C.W. Garland and J.R. Wilt, J.Chem.Phys., 36 (1962) 1094.
4. J.G. Bullitt and F.A. Cotton, Inorg.Chim.Acta., 5 (1971) 637.
5. K. Klanderman and L.F. Dahl, unpublished results mentioned in L.R. Bateman, P.M. Maitlis and L.F. Dahl, J.Am.Chem.Soc., 91 (1969) 7292.
6. J. Coetzer and G. Gafner, Acta.Crystallogr., Sect.B., 26 (1970) 985.
7. J.J. Bonnett, Y. Jeanin, P. Kalck, A. Maissonat and R. Poilblanc, Inorg.Chem., 14 (1975) 743.
8. J.A. Ibers and R.G. Snyder, Acta.Crystallogr. 15 (1962) 923.
9. M.D. Curtis, W.M. Butler and J. Greene, Inorg.Chem., 17 (1978) 2928.

10. J.G. Norman and D.J. Gmur, J.Am.Chem.Soc., 99 (1977) 1446.

11. A. Serafini, R. Poilblanc, J.-F. Labarre and J.-C. Barthelat, Theor.Chim.Acta, 50 (1978) 159.

12. T.H. Gan, J.B. Peel and G.D. Willett, Chem.Phys.Lett., 48 (1977) 483.

13. J.A. McCleverty and G. Wilkinson, Inorg.Synth, 8 (1966) 211.

14. E. Nagy-Fëlsobuki and J.B. Peel, J.Chem,Soc. Faraday 2, 74 (1978) 1927.

15. B.R. Higginson, D.R. Lloyd, P. Burroughs, D.M. Gibson and A.F. Orchard, J.Chem.Soc.Faraday 2, 69 (1973) 1659.

16. T.F. Block and R.F. Fenske, J .Am.Chem.Soc., 99 (1977) 4321.

17. H. van Dam, D.J. Stufkens and A. Oskam, Inorg.Chim.Acta., 31 (1978) L377.

18. L.S. Cederbaum, W. Domcke, W. von Niessen and W. Brenig, Z.Physik B21 (1975) 381.

19. M. Texter, I.D. Gay and R. Mason, Proc.Roy.Soc.Lond.A. 356 (1977) 37.

20. H.B. Gray, in Electrons and Chemical Bonding, Benjamin, New York,1964, Chapter 2.

21. F. Carnovale, T.H. Gan and J.B. Peel, Aust.J.Chem., 32 (1979) 719.