Electron Spectroscopy of Platinum Complexes

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Abstract: A number of complexes of platinum, in which the metal is in a formally low oxidation state, have been investigated by the ESCA technique. Binding energies of Pt 4f$_{7/2}$ electrons were obtained and interpreted in terms of the degree of oxidation of the metal by assuming that within the series of complexes the platinum 4f$_{7/2}$ binding energies were dependent only on the electronic charge transferred from the metal to the ligand. Although the model is extremely simple, relative oxidation states of platinum in the complexes, as determined from the binding energy data, are sensibly ordered. A choice of two model compounds has enabled quantitative estimates to be made of the charge transferred in individual cases. Using arguments originally developed by Walsh for predicting molecular geometries of free molecules, correlations have been attempted between the charge transferred to the ligand and its anticipated geometry; where possible such predictions have been compared with crystallographic data. Core-level energies determined for certain of the atoms comprising the ligands confirm that coordination to the metal results in a significant charge transfer from the metal to the ligand.

Changes in the molecular geometry of molecules upon coordination to metals was conclusively demonstrated by Sly[2] 11 years ago. More recently the nonlinearities of coordinated diphenylacetylene[3a] and carbon disulfide[3b] in the complexes $(PPh_3)_2Pt(PhC{\equiv}CPh)$ and $(PPh_3)_2Pt(CS_2)$ have provoked considerably more interest following the observation by Mason[4] that the geometries of the coordinated molecules correspond rather closely to those obtaining in certain spectroscopically observable states of the free molecules. Careful analysis of the ir spectra of $(CO)_6Co_2(C_2H_2)$ and its deuterated analogs[5] and measurement of ^{13}C–H coupling constants[6] in $(PPd_3)_2Pt(H^{13}C{\equiv}{}^{13}CH)$ and $(PPd_3)_2Pt(H_2{}^{12}C{=}{}^{13}CH_2)$, where PPd$_3$ = perdeuteriotriphenylphosphine, illustrate alternative techniques, free from possible crystal effects, for determining molecular perturbations attending coordination. Although the evidence for such perturbations is now overwhelming, virtually nothing is known about the electron reorganization between ligand and metal which leads to the observed changes in ligand geometries.

In a pioneer study of this problem, Blizzard and Santry[7] have recently calculated variations in the CCH angle which would accompany (a) electronic charge transferred to antibonding π orbitals in acetylene and (b) charge removed from bonding π orbitals and simultaneously added to antibonding π orbitals. A theoretical study[8] of acetylenic and olefinic complexes of platinum has, by means of Löwdin and Mulliken population analyses, yielded estimates of charge distributions within such molecules.

ESCA[9a] has shown itself to be a sensitive technique for determining atomic core-level binding energies in a wide variety of simple and complex molecules.[10] It is well established that core-level binding energies are dependent, *inter alia*, upon the charge associated with the atom in question, and it seemed of interest to attempt to obtain quantitative information on metal–ligand charge transfer in a series of metal complexes. The hazards of relating chemical shifts solely to changes in the localized charge on the atom (*i.e.*, ignoring neighboring-atom potentials) have been discussed previously. However, within a closely related series of compounds such as we have chosen, a simple charge/shift approach can be applied with confidence. We report here variations in the 4f$_{7/2}$ binding energy of platinum in complexes having the general formula $(PPh_3)_2PtL$ (L = 2PPh$_3$, C$_2$H$_4$, PhC≡CPh, CS$_2$, O$_2$, 2Cl).

Since much of our discussion concerns ground-state molecular geometries, it is worth pointing out that X-ray photoemission follows the Franck–Condon principle, since the process takes place in a much shorter time (10^{-16} sec) than the period of molecular vibrations. Although the nuclear framework of the molecule probably does not change during photoemission, it does not follow that it has maintained the ground-state electron distribution, *i.e.*, that Koopmans' theorem is applicable. However, removal of a 4f electron from platinum(0) increases the effective nuclear charge felt by the valence electrons by only $\sim$10% (Slater's rules), and since we are concerned with *differences* in measured *core-level* binding energies, we assume, as have others,[9b] that the ESCA shifts are determined essentially by the valence electron distribution in the electronic ground state of the neutral molecule.

Experimental Section

Binding energies were obtained using a redesigned iron-free magnetic instrument, the basic details of which can be found else-

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[1] (a) University of Toronto; (b) University of Uppsala.

[2] W. G. Sly, *J. Amer. Chem. Soc.*, **81**, 18 (1959).

[3] (a) J. O. Granville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, P9 (1967); (b) M. C. Baird, G. Hartwell, R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*, 92 (1967).

[4] R. Mason, *Nature (London)*, 217, 543 (1968).

[5] Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

[6] C. D. Cook and K. Y. Wan, *J. Amer. Chem. Soc.*, **92**, 2595 (1970).

[7] A. C. Blizzard and D. P. Santry, *ibid.*, **90**, 5749 (1968).

[8] J. H. Nelson, K. S. Wheelock, L. C. Cusacks, and H. B. Johassen, *ibid.*, **91**, 7005 (1969).

[9] (a) ESCA = electron spectroscopy for chemical analysis; (b) M. Barber and D. T. Clark, *Chem. Commun.*, 23 (1970).

[10] (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA; Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967; (b) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North Holland, Amsterdam, 1969, p 104.

where.[10] Samples of the complexes, which were all crystalline powders of reasonable stability in air, were finely ground and pressed into a copper mesh. Electron emission was achieved by the Mg K$\alpha_{1,2}$ line (1253.6 eV) and all samples were allowed to attain the ambient spectrometer temperature. Visual examination of the sample following irradiation in the spectrometer showed little radiation damage to have occurred; for those compounds which were noticeably darkened spectral lines were obtained from fresh samples of the complex irradiated in the shortest possible time commensurate with statistical accuracy.

The following five complexes were prepared by published procedures:[11–14a] $(PPh_3)_4Pt$, $(PPh_3)_2PtCl_2$, $(PPh_3)_2Pt(CS_2)$, $(PPh_3)_2Pt(C_2H_4)$, and $(PPh_3)_2Pt(O_2)$. $(PPh_3)_2Pt(PhC{\equiv}CPh)$[15] was prepared by reduction of $(PPh_3)_2PtO_2$ with $NaBH_4$ in the presence of $PhC{\equiv}CPh$, using the procedure reported[14] for the preparation of $(PPh_3)_2Pt(C_2H_4)$. $(PPh_3)_2(PtSO_2)$, which has been reported[16] previously without preparative details, was synthesized in the following manner.

Sulfur dioxide was passed slowly through a solution of $(PPh_3)_2Pt(C_2H_4)$ (1.0 g) in 30 ml of deoxygenated benzene-hexane (9:1). Crystals precipitated rapidly and were separated by decantation in a stream of nitrogen. After washing with hexane, the crystals were pulverized and warmed (50–60°) on a water bath in a stream of nitrogen. The apple-green product (0.9 gm) is air stable. *Anal.* Calcd for $C_{36}H_{30}O_2P_2SPt$: C, 55.17; H, 3.83; S, 4.09. Found: C, 54.92; H, 3.94; S, 4.68.

Results

Figure 1 shows the platinum $4f_{7/2}$ binding energies for the series of complexes investigated, together with other core-level energies of interest, in particular, the phosphorus 3p level. Chemical shifts were determined by relating all energies to the carbon 1s level of the triphenylphosphine ligand present in all the complexes; it would seem reasonable to assume that this binding energy remains constant throughout the series. By means of this procedure possible errors resulting from charging of the samples are obviated. Absolute binding energies which, because of the insulating nature of the sample are necessarily less precise, have been calculated using values of 285.0 eV for the carbon 1s binding energy and 3.7 eV for the spectrometer work function. The complex $(PPh_3)_2PtSO_2$ was found to be unstable in the spectrometer, and a broad unresolved line (half-height width, 2.5 eV) resulted for the Pt $4f_{7/2}$ electrons. Examination of the S 2p level, however, yielded two resolved peaks corresponding to S 2p binding energies of 166.5 and 168.5 eV. These values compare well with S 2p binding energies recently obtained[17] for ions of the type $R{-}SO_2^-$ and SO_4^{2-} (166.5 and 168.9 eV, respectively), and it is evident that oxidation of the SO_2 complex in the presence of high-energy radiation has occurred, yielding the sulfato derivative $(PPh_3)_2PtSO_4$. Easy oxidation of the SO_2 complex has already been reported.[16]

Interpretation of Data. In a number of earlier publications[9,10] the variation of atomic core-level binding energies with the state of oxidation of the atom has been clearly demonstrated. In the present investigation the chemical shift of the platinum $4f_{7/2}$ level suggests that the state of oxidation of platinum increases with varying L in the series $PPh_3 < PhC_2Ph \sim C_2H_4 < CS_2 < O_2 < Cl_2$.

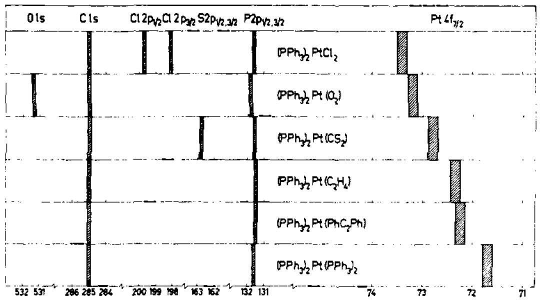

Figure 1. Core-level binding energies.

In order to achieve our objective of relating the chemical shift data to metal–ligand (L) electron transfer, it is necessary to first establish that the phosphorus–platinum interaction does not change significantly throughout the series. As can be seen from Figure 1, the phosphorus 2p binding energies are essentially constant for the complexes studied, a fact which lends the strongest support to the above premise. Additional, albeit less precise, evidence for constancy in the Pt–PPh_3 interaction is provided by Pt–P bond lengths, and values for a number of platinum phosphine-containing complexes are contained in Table I. Despite changes of the phosphine substituent and in the formal oxidation state of platinum, the Pt–P bond lengths for "typical" complexes (ref *a–e* of Table I) fall in the range 2.26 ± 0.02. It will be noticed that incorporation of unusually good π-accepting ligands such as tetracyanoethylene and carbon monoxide in phosphine–platinum complexes (ref *f–i* of Table I) results in a pronounced lengthening of the Pt–P bond. This effect is sensible in view of Venanzi's recent conclusions[18] concerning the nature of the platinum–phosphine bond and supports, we feel, our proposal of invariance.

Table I. Platinum–Phosphorus Bond Lengths

Complex	Pt–P bond lengths, Å	Ref
$(PPh_3)_3Pt$	2.25–2.28	*a*
$(PMe_3)_2PtCl_2$	2.24–2.26	*b*
$(PPh_3)_2Pt(PhC{\equiv}CPh)$	2.27–2.28	*c*
$(PPh_3)_2PtCO_3$	2.24	*d*
$(PPh_3)_2PtO_2$	2.25–2.28	*e*
$(PPh_3)_3Pt(CO)$	2.35–2.37	*f*
$(PPh_3)_3Pt(CO)$	2.33–2.35	*g*
$(PEt_3)_2Pt(CO)(CO)^+$	2.35–2.36	*h*
$(PPh_3)_2Pt[C_2(CN)_4]$	2.29–2.30	*i*

[a] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966). [b] G. G. Messmer, E. S. Amman, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967). [c] Reference 2. [d] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Commun.*, 408 (1967). [e] T. Kashiwagi, N. Yasouka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *ibid.*, 743 (1969). [f] V. G. Albano, P. L. Bellon, and M. Sansoni, *ibid.*, 889 (1969). [g] V. G. Albano, G M. Basso-Ricci, and P. L. Bellon, *Inorg. Chem.*, **8**, 2109 (1969). [h] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 3360 (1967). [i] C. Pannatoni, G. Bombieri, U. Belluco, and W. H. Baddley, *ibid.*, **90**, 798 (1968).

Two of the complexes studies, $(PPh_3)_4Pt$ and $(PPh_3)_2PtCl_2$, are widely accepted as being examples of plat-

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(11) L. Malatesta and C. Carriello, *J. Chem. Soc.*, 2323 (1958).

(12) J. C. Bailar and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

(13) M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).

(14) (a) J. Chatt, B. L. Shaw, and A. A. Williams, *ibid.*, *A*, 3269 (1962); (b) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(15) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc., London*, 208 (1957).

(16) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **89**, 3066 (1967).

(17) B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, manuscript in preparation.

(18) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968).

inum in oxidation states zero and two, respectively; the state of oxidation of platinum in the remainder is a much more controversial problem. As Nyholm and Tobe[19] have pointed out, the oxidation state formalism is simply an artificial aid to systematization, and time should not be spent trying to make it work in inappropriate cases. Jørgensen[20] has discussed in detail the problems attending the construction of a suitable formalism and has introduced several new and interesting concepts. In this paper, however, we adopt the following simple convention. In the model compounds $(PPh_3)_4Pt$ and $(PPh_3)_2PtCl_2$ we assume that the metal transfers zero and two electrons, respectively, to the L ligand ($2PPh_3$ and 2Cl); we further assume that the Pt $4f_{7/2}$ binding energies reflect *only* the charge transferred to the L ligand and that the binding energies have a linear dependence on the metal–L charge transfer.

The convention has some drawbacks, the most serious of which relates to the assumptions concerning the model compounds. It is evident that the metal does not transfer two units of charge to the chlorine atoms, the covalency of the Pt–Cl bond in $PtCl_6^{2-}$ having been estimated[21] from an nqr measurement to be in the range of 30–50%.

The assumed electrical neutrality of the metal in $(PPh_3)_4Pt$ is probably more realistic; chemically, the complex (which dissociates in solution) reacts as a nucleophile rather than an electrophile, and close similarities have been observed between heterogeneous reactions of the bulk metal and homogeneous reactions of the complex.[22] Moreover, the Pt $4f_{7/2}$ binding energy in this complex (71.7 eV) is in tolerable agreement with that recently found in metallic platinum (71.2 eV). Comparison of binding energies derived from identical levels in metals and insulators is not strictly valid (since in the latter case the sample and spectrometer are not necessarily[23] in electrical equilibrium), but the agreement is encouraging.

Despite these reservations we find our convention useful in that it is capable of rationalizing in a conceptually simple manner the observed changes in ligand geometry which attend coordination. The reverse procedure of estimating charge transfer from crystallographically determined ligand distortions has been used most effectively by Ibers[24] and his coworkers in connection with the coordinated oxygen molecule. The alternative and perhaps more realistic approach to ligand distortions used by Mason,[4] that of transfer of charge from bonding to antibonding orbitals using the intermediacy of the metal atom, would necessitate interpretation of the binding energy data in terms of differences between σ and π contributions; this appeared to be an impossible proposition.

Using the procedure outlined above, estimates have been made of the metal–ligand electron transfer for the series of complexes studied, and these are contained in Table II.

Table II. Estimated Metal-Ligand Charge Transfer

Ligand L	Metal–ligand charge transfer, electrons
$(PPh_3)_2$	0.0[a]
PhC_2Ph	0.7 ± 0.2
C_2H_4	0.8 ± 0.2
CS_2	1.3 ± 0.2
O_2	1.8 ± 0.2
Cl_2	2.0[a]

[a] Assumed values; see text.

Discussion

(a) $(PPh_3)_2Pt(PhC{\equiv}CPh)$ and $(PPh_3)_2Pt(H_2C{=}CH_2)$. Acetylenic complexes of this type have been the subjects of a number of studies, including kinetic,[25] crystallographic,[3a] spectroscopic,[6] and theoretical,[8] since they were first reported by Chatt[15] and coworkers in 1957; the considerably less stable olefinic analogs[16] have received little attention. The overriding concern throughout these investigations has been with the nature of the metal–ligand bond, although recently attention has shifted somewhat to the problem of estimating ligand distortions and their possible origin, using an idealized "free-ligand" model.[7] The primary problem, simply put, is whether to represent an acetylene complex, for example, as being a metallocyclopropene derivative (two C–Pt σ bonds; platinum(II) complex), or whether a better representation is that of a π adduct of platinum(0). There has recently been a shift on the part of some[26] toward a more flexible representation of the bonding in such molecules, but the pull toward an "either/or" description[8] is still strong. The Dewar–Chatt–Duncanson[27] representation of the bonding between unsaturated ligands and metal ions, and a recent embellishment[8] of it, can accommodate any reasonable (in the range 0–2), fractional, or integral oxidation state of platinum, since the net electron transfer will depend on the relative magnitudes of the σ and π contributions. The binding energies of the platinum $4f_{7/2}$ electrons in these complexes are similar and correspond, following our convention, to the net transfer from metal to ligand of 0.7 electron in the acetylenic complex and 0.8 electron in the olefinic. These values, which, for reasons discussed earlier, are probably overestimates, indicate that the complexes are better (but not precisely) described as platinum(0) complexes rather than derivatives of platinum(II), a view which two other groups[8,26b] have recently expressed. Furthermore, these figures confirm the importance of the π (metal to ligand) interaction, the existence of which has been postulated and invoked on a number of occasions but for which convincing proof has been lacking. This comment on metal–ligand back-bonding is of course generally true for our series of Lewis acid–base complexes, since an increasing positive charge on platinum can only result

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(19) R. S. Nyholm and M. L. Tobe, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963).

(20) C. K. Jørgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, Berlin, 1969.

(21) D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, **82**, 5783 (1960).

(22) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

(23) However, as pointed out previously (ref 10a, p 36), if the sample is distributed as a thin film on a metallic backing, there are usually a sufficient number of free charges present, as a result of the X-radiation, to ensure electrical equilibrium.

(24) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(25) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

(26) (a) W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 3705 (1968); (b) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(27) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

from an increasingly effective transfer from the filled metal d orbitals to high-energy orbitals on the ligand.

Walsh[28a] discussed some years ago the effect on molecular geometry of increasing charge on the molecule and in a later summary[28b] presents the postulate that the shape of the first excited state of a molecule resembles that of the ground state of the similar molecule containing $(n + 1)$ or $(n + 2)$ electrons. For example, CS_2 (16 electrons), linear in its ground state, should be bent in its lowest excited state and resemble NO_2 (17 electrons; ONO angle, 134°); indeed the SCS angle in the $^3A_2$ state of CS_2 is reported[29] to be 135°. Thus it would appear that although the extra electron in the triatomic system quoted above is accommodated in a delocalized nonbonding MO, the stereochemical result is similar to that observed when an electron is promoted to an antibonding orbital and a hole is created in a lower energy MO. The stereochemical inactivity of a hole in a bonding MO has recently been demonstrated[7] for the C_2H_2 molecule.

A second empirical rule propounded by Walsh[27b] concerns the numerical importance of electrons in determining molecular geometries, and states that molecules (or molecular ions) having equal numbers of atoms will be geometrically equivalent when they are isoelectronic.

Employing the Walsh approach, it is therefore possible to relate ligand distortion to increased electron density on the ligand, which in turn can be related to binding energies of core-level electrons on the metal. At the same time we implicitly preserve the attractive excited-state concept,[4] since the anticipated stereochemical changes, for simple noncoordinated molecules at least, are equivalent whichever approach one uses.

Calculations[7] show that the transfer of 0.7 electron to antibonding orbitals of an acetylenic ligand should result in an angular distortion of 40° (trans configuration); it has been shown experimentally[30] that the lowest excited state of acetylene has a CCH angle of 120°, again with a trans configuration.

The ESCA results for the acetylenic ligands would seem therefore to be in perfect agreement with crystallographic[2] and nmr[6] studies of coordinated acetylenes, both of which indicate 40° distortions from linearity of the ligand. However, the 40° angular distortions in $(PPh_3)_2Pt(PhC{\equiv}CPh)$ and $(PPh_3)_2Pt(CH{\equiv}CH)$ occur in cis configurations of the ligands rather than trans, and although the energies required to excite C_2H_2 to trans and cis configurations have been shown[31] to be rather close, the validity of a simple comparison is doubtful. Blizzard and Santry[7] have calculated cis angular distortions resulting from charge addition to antibonding π orbitals, and according to their figures a 0.7-electron transfer would cause a 20° angular distortion of the ligand. This is small, disturbingly so in view of our probable tendency to overestimate the charge transferred, but in the absence of refined crystallographic data, particularly with regard to nonbond interactions in the crystal, further discussion would not be profitable.

A calculation based on ^{13}C–H coupling constants of bond angles of ethylene in the complex $(PPh_3)_2Pt(C_2H_4)$ has demonstrated[6] nonplanarity of the molecule and HCH angles of 115°. There are no calculations of the Blizzard and Santry type with which our 0.8-electron ligand transfer can be compared. However, using the Walsh approach the excited state of C_2H_4 (stereochemically equivalent to a one-electron transfer) should resemble the ground state of hydrazine; for 1,2-dimethylhydrazine, nonplanarity and 110 ± 4° bond angles have been reported.[32] Although the data are too crude for meaningful comparisons, it would seem that the ESCA, nmr, and crystallographic results are not inconsistent.

Finally it is worth noting that the Pt $4f_{7/2}$ binding energies show very similar electron redistributions in the acetylenic and ethylene complexes, a fact which might have been anticipated using the orbital-energy-matching approach of Baddley[26a] and Greaves, Lock, and Maitlis.[26b]

(b) $(PPh_3)_2Pt(CS_2)$. Relatively few complexes are known which contain coordinated CS_2, but fortunately their novelty has prompted structural studies of two of them. The linearity of CS_2 is removed in both of the complexes $(PEt_3)(CS_2)$[33] and $(PPh_3)_2Pt(CS_2)$,[3] the SCS angles being 128 and 136°, respectively. The CS_2^- ion would, according to Walsh's rules, be expected to have the geometry of NO_2 (ONO angle reported[34] to be 134°), and the close similarity of the geometries of the coordinated molecule to this value suggests that essentially one electron has been transfered to CS_2 in the two cases. The value which we obtain for the metal–ligand transfer, namely 1.3 electrons, is in good agreement with this concept, bearing in mind once again that our value is probably an overestimate. Although the formulation[33] of the tertiary phosphine–CS_2 complex as a zwitterion of a quaternary phosphonium derivative of dithioformate $[(PEt_3)^+(CS_2)^-]$ appears intuitively reasonable, the formulation of the platinum derivative in like manner, which our results demand, is somewhat more novel. The dissimilar manner in which CS_2 is bound to the phosphine and to platinum (monodentate in the former, bidentate in the latter) unfortunately clouds the essential similarity of the two compounds; however, we regard the functioning of CS_2 as a bidentate ligand in the platinum complex as arising simply from the coordinative unsaturation of the putative three-coordinate derivative and the high donor ability of the adjacent sulfur atom. Interestingly, the SO_2 molecule in $(PPh_3)_2Pt(SO_2)$ appears on the basis of its ir spectrum to be bound only through sulfur reflecting, no doubt, the lower affinity of oxygen for the electron-rich metal. We finally note that our findings are in line with Schrauzer's recent comments[35] concerning "odd" ligands and their tendency to exist as monoanions when coordinated to Lewis bases.

(c) $(PPh_3)_2PtO_2$. Following Vaska's discovery[36] that the complex $(PPh_3)_2Ir(CO)(Cl)$ was able to fix molecular oxygen, interest in discovering alternative paradigms of the hemoglobin system has been high. The crystallographic studies by Ibers[24] and coworkers of a series of

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(28) (a) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); (b) "Advances in Stereochemistry," Vol. 1, Butterworths, London, 1954, p 1.

(29) B. Kleman, *Can. J. Phys.*, **41**, 2034 (1963).

(30) C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).

(31) H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 792 (1967).

(32) W. Beamer, *J. Amer. Chem. Soc.*, **70**, 2979 (1948).

(33) (a) T. N. Margulis and D. H. Templeton, *ibid.*, **83**, 995 (1961); *J. Chem. Phys.*, **36**, 2311 (1962); (b) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 547 (1963).

(34) G. R. Bird, *J. Chem. Phys.*, **25**, 1040 (1956).

(35) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

(36) L. Vaska, *Science*, **140**, 809 (1963).

related iridium oxygen-carrying complexes resulted in the working hypothesis, based on O–O bond lengths, that irreversibility of oxygen uptake by metal ions can be equated with a peroxy type of coordinated oxygen (O–O length of 1.49 Å in the O_2^{2-} ion), whereas the reversible systems contain oxygen more nearly in its molecular state (O–O length of 1.21 Å in O_2 gas).

Oxygen in $(PPh_3)_2Pt(O_2)$ is irreversibly bound,[37] and although a "sensible" O–O distance of 1.45 Å was found by workers in Tokyo[38] for the benzene-solvated complex, the Toronto group[39] reported 1.26 ± 0.05 Å for the corresponding toluene-solvated molecule. More recently we have found a O–O bond length of 1.50 Å in the complex $(PPh_3)_2PtO_2 \cdot 2CHCl_3$, but have observed a very close approach of the chloroform proton to the bonded oxygen molecule raising the possibility of hydrogen-bond lengthening of the O–O bond.[40] A reinvestigation of the toluene adduct is evidently called for, but despite the limited accuracy, we have no grounds at the moment for supposing that our earlier result was not meaningful.

The ESCA measurements on the oxygen complex show that a maximum of about 1.8 electrons are transferred to the ligand. Table III shows the variation of the O–O bond length with increasing negative charge on the O_2 molecule (O_2^+, O_2, O_2^-, O_2^{2-}), and interpolation of these data yields an anticipated maximum O–O length of about 1.4 Å. If, as generally seems to be the case, we have overestimated the charge transferred by about 0.4 electron, then an anticipated O–O bond length of about 1.35 Å is probably a more realistic estimate. In both the crystallographic structural determination and in the obtaining of the ESCA spectrum, this compound has been distinctly uncooperative, mainly as a result of its high reactivity, a reactivity which is apparently enhanced by X-radiation. It is probably significant that the measured P 2p binding energy in this complex is somewhat higher than those obtained for the other members of the series, and it may be that autoxidation of the phosphine ligand has led to a less precise determination of the Pt $4f_{7/2}$ binding energy than we appear to have achieved in the other cases.

Table III. O–O Bond Lengths

Molecule	O–O bond length, A[a]
O_2^+	1.12
O_2	1.21
O_2^-	1.28
O_2^{2-}	1.49

[a] Taken from L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18**, S9s (1965).

(d) General. Although the arguments developed above rest on variations in the Pt $4f_{7/2}$ binding energies, it is of obvious interest to examine the effect of coordination on core-level binding energies of ligand atoms. If the chemical shifts determined for platinum reflect only the ligand–metal transfer, and this is our premise, then to maintain electrical neutrality the ligand atom should show an opposite reductive shift to lower binding energies. Charge added to polynuclear unsaturated ligands is delocalized over the molecule, and this makes a quantitative comparison of the degree of reduction of the ligand using previously developed[10] binding energy–charge correlations impossible, since we have not been able to measure a suitable core-level binding energy for every atom constituting the ligand. More importantly, attempts at a precise comparison would not be in order, since the reported degrees of oxidation of platinum are relative values based on our choice of model compounds, whereas the binding energy–charge data for selected ligand atoms with which we wish to compare are absolute in the sense that either the Pauling electronegativity scale or the CNDO computational approach was used in the calculations of the atomic charge. A semiquantitative comparison is, however, interesting, and the data, although limited, lend support to the charge-transfer effects discussed in the foregoing sections.

The ESCA spectra of a large number of solid, covalent, sulfur-containing compounds have been obtained[17] in the last few years, and a correlation between S 2p binding energies and charge parameter, q_p, has been established. The S 2p binding energy recorded for the complex $(PPh_3)_2Pt(CS_2)$, 162.8 eV, indicates that the sulfur is in a reduced state, the binding energy being intermediate between that found[17] in CS_2 (163.9 eV) and in the S^{2-} ion (162.0 eV).

In general it has proved difficult to detect C 1s electrons emitted from carbon atoms associated with the L ligands, owing to the high intensity of the line produced by the 36 carbons of the triphenylphosphine ligands. However, in the spectrum of the complex $(PPh_3)Pt(C_2H_4)$ a peak clearly attributable to electron emission from the olefin can be detected on the low-energy flank of the main C 1s electron line, and by deconvolution[10b] it can be shown to differ in energy by 1.8–1.9 eV. Shifts toward lower binding energies of a similar magnitude have been recorded for C 1s lines in a series of carbides[41] and were interpreted in terms of metal–carbon charge transfer. Comparison of our results with these, and with the CNDO charge–binding energy correlation curve, established[42] for numerous carbon-containing compounds, confirms that the olefinic carbon atoms in $(PPh_3)_2Pt(C_2H_4)$ are negatively charged.

Comparison of the O 1s binding energy determined for the complex $(PPh_3)_2Pt(O_2)$ with data compiled for oxygen-containing compounds shows that the O 1s binding energy in the complex (531.2 eV) is about as low as any thus far recorded, falling between those found[17] in the SO_3^{2-} ion (531.9 eV) and in a series[43] of vanadium and tungsten oxides (530.6 eV). A charge-binding energy correlation curve is not yet available for covalent oxygen-containing solids; the lack of such data and the absence of individual measurements on peroxy- or superoxy-type oxygen precludes further comment.

Finally, we note that Cl $2p_{3/2}$ binding energies in $(PPh_3)_2PtCl_2$ and NaCl are very similar (198.1 and 198.5

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eV, respectively). The higher binding energy of 2p electrons in Cl^- exemplifies the difficulties which arise when attempting to compare binding energies of identical atoms in ionic and covalent compounds. The influence of the crystal field on binding energies has been dealt with elsewhere,[10,44] and it is only necessary here to reiterate the fact that the lattice type has a significant and complex effect on measured core-level energies.

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Metal–Metal Bond Equilibria in Aqueous Solution. I. Zinc Tetracarbonylferrates(–II)[1]

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Abstract: The reaction of the carbonylferrate(−II) anions $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with zinc(II) was studied potentiometrically. On the basis of equilibrium measurements of hydrogen ion concentrations at 20° and a total normality of 1.0 ($NaClO_4$), the equilibrium constants of the following reactions have been evaluated: (A) $Fe(CO)_4^{2-} + Zn^{2+} \rightleftharpoons ZnFe(CO)_4$, (B) $HFe(CO)_4^- + Zn^{2+} \rightleftharpoons ZnHFe(CO)_4^+$, (C) $ZnFe(CO)_4 + Zn^{2+} \rightleftharpoons Zn_2Fe(CO)_4^{2+}$, (D) $2ZnFe(CO)_4 + 2H_2O \rightleftharpoons [HOZnFe(CO)_4]_2^{2-} + 2\,H^+$. The values of the equilibrium constants are, respectively, $(4.0 \pm 0.8) \times 10^8\ M^{-1}$, $21 \pm 3\ M^{-1}$, $30 \pm 3\ M^{-1}$, and *ca.* $2 \times 10^{-16}\ M$. The acid dissociation constants of $H_2Fe(CO)_4$ were redetermined at 20° and 1 *M* $NaClO_4$. $pK_a(H_2Fe(CO)_4) = 4.00 \pm 0.01$; $pK_a(HFe(CO)_4^-) = 12.68 \pm 0.04$.

Heavy-metal derivatives of iron carbonyl hydride of the type $MeFe(CO)_4$, where Me is Hg(II),[2] Cd(II)[3] or Pb(II),[4] are, contrary to the corresponding monomeric derivatives of cobalt carbonyl hydride, *e.g.*, Hg $[Co(CO)_4]_2$,[5] insoluble and very likely polymeric[6] species. An analogous zinc derivative has, hitherto, not been obtained. Hieber and Fack[7] prepared the ammine complex $(NH_3)_3ZnFe(CO)_4$, which dissolves in methanol to form weakly conducting solutions. An earlier observation[3] suggests the existence of a water-soluble cadmium derivative. The ammine complex $(NH_3)_2CdFe(CO)_4$ dissolves in aqueous acetic acid without liberation of the carbonyl hydride. $CdFe(CO)_4$ is precipitated when this solution is heated to boiling.

With the aim of elucidating the nature of such soluble metal carbonyl species, it was decided to investigate further the reaction of the carbonylferrate anions $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with heavy metal ions. It was hoped that formation constants of the respective metal–metal-bonded species could, eventually, be obtained. In this paper we report the results of a potentiometric study of the reaction of the carbonylferrate anions with zinc(II) in aqueous solution.

Experimental Section

All of the manipulations with the highly oxygen-sensitive carbonylferrate solutions were performed under an atmosphere of high-purity nitrogen. All solutions were made up using water triply distilled in an all-glass still. The concentration of hydrolytic impurities was evaluated from the change in pcH ($= -\log\ [H^+]$) on the addition of increasing amounts of acid and base.[8] The values given below and used in the calculations of the equilibrium constants refer to the pcH range 8.2–5.5 (mean initial and final pcH of the experiments with $Na[HFe(CO)_4]$). All solutions were standardized to within ±0.1% according to accepted methods.

A 4.5 *M* stock solution of sodium perchlorate was prepared according to Biedermann[9] and adjusted to pcH 6–6.3 at 1 *M*. The concentration of hydrolytic impurities in the deaerated 1 *M* solution was $(5 \pm 2) \times 10^{-6}\ M$. A 0.50 *M* solution of zinc perchlorate was prepared from reagent grade zinc oxide and perchloric acid, so that after tenfold dilution with 1 *M* $NaClO_4$ the pcH was 5.5. Hydrolytic impurities were within the limits indicated for $NaClO_4$ alone. The two solutions were used in the titration experiments with $Na[HFe(CO)_4]$. In the experiments with $Na_2[Fe(CO)_4]$, solutions were used which were, respectively, 0.25 and 0.0625 *M* in zinc and 1.00 *M* in $NaClO_4$.

Solutions of sodium hydridotetracarbonylferrate(−II) were prepared by the procedure described earlier,[10] slightly modified to ensure a low carbonate content and absence of dissolved $Fe(CO)_5$. Freshly distilled $Fe(CO)_5$ (1.95 g, 9.95 mmol), measured with a Gilmont micrometer syringe, was added to 100 ml of an aqueous solution containing 11.00 mmol of $Ba(OH)_2$ and 8.00 mmol of NaOH, placed in a 150-ml Schlenk tube. The tube was shaken for 3 hr

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