On the Charge Distribution in Complexes

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Dipole moment, *X*-ray photoelectron (*X*-p.e.) spectroscopic, and electrochemical measurements are evaluated as means of determining charge distribution in complexes. The first is of limited value because of the inability to determine individual bond moments. *X*-P.e. spectroscopy is of most general application but limited by lack of sensitivity. Redox measurements can only be interpreted clearly where there are no π-bonding ligands. The data are consistent with tertiary phosphines and chloride ions being good electron donors, chlorine and nitrogen atoms being strongly electron withdrawing, and the so-called electron-donor ligands N_2, CO, and NO (even formal NO^+) being, in fact, electron withdrawing. On the other hand the formally anionic hydride ligand is very strongly electron donating, being only slightly negative in its complexes.

THE distribution of charge in a complex is believed to exert a considerable influence on the reactivity and mode of reaction of both the metal ion and its ligands. We have been especially concerned with how charge distribution affects the reactivity of co-ordinated dinitrogen. To this end we have applied three techniques, namely dipole-moment determination, *X*-ray photoelectron (*X*-p.e.) spectroscopy, and electrochemistry, to a series of complexes, mainly of rhenium, containing chloride, tertiary phosphines, and ligands such as dinitrogen, carbon monoxide, and nitrogen oxide, in order to determine the charge distribution.

None of the techniques gives absolute values of atomic charges, nor, since each measures a different quantity and gives different information, need they agree. Thus, dipole moment is a measure of electrical asymmetry in a molecule, binding energy reflects the potential in which the relevant electron is moving, and redox potential is the potential required to transfer an electron to or from a molecular redox orbital relative to a standard electrode. Each of these obviously depends on relevant atomic charges, but the dependence is not simple and measured

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values are generally perturbed by crystal or solvent effects. We thus need to define conditions under which the results from all three techniques give a meaningful correlation.

RESULTS AND DISCUSSION

Dipole-moment Measurements.—Table 1 shows dipole moments of a series of complexes derived from transition-metal ions, tertiary phosphines, and chloride ions only. These moments can be considered as the resultants of vectorial components lying along the bond axes; thus the moment of *cis*-$[PtCl_2(PEt_3)_2]$ (10.7 D)[1,2] ($D \approx 3.33 \times 10^{-30}$ Cm) can be considered to result from two component P–M–Cl group moments at right angles, each of 7.6 D. Octahedral complexes have moments which can be similarly resolved, although in some cases due to axial symmetry the P–M–Cl group moment along the axis is measured directly. All the octahedral P–M–Cl group moments lie in the range 6.6 ± 0.6 D. Evidently the group moment is relatively insensitive to the metal and to the type of tertiary phosphine.

TABLE 1

Some P–M–Cl group moments (D)

Complex	Observed dipole moment	P–M–Cl group moment
trans-$[Pt(PEt_3)_2Cl_2]$	10.7 [1,2]	7.6
mer-$[Ru(PEt_2Ph)_3Cl_3]$	6.9 [a]	6.9
mer-$[Rh(PEt_2Ph)_3Cl_3]$	7.3 [b]	7.3
mer-$[Rh(PEt_3)_3Cl_3]$	7.0 [b]	7.0
mer-$[Re(PEt_2Ph)_3Cl_3]$	6.3 [c]	6.3
mer-$[Ir(PEt_3)_3Cl_3]$	6.9 [d]	6.9
cis-$[Ru(Et_2PCH_2CH_2PEt_2)_2Cl_2]$	9.8 [e]	7.0
cis-$[Ru(Ph_2PCH_2CH_2PPh_2)_2Cl_2]$	9.5 [e]	6.8
cis-$[Os(Et_2PCH_2CH_2PEt_2)_2Cl_2]$	9.3 [e]	6.6
cis-$[Os(Ph_2PCH_2CH_2PPh_2)_2Cl_2]$	8.3 [e]	5.9

[a] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466. [b] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508. [c] J. Chatt and A. G. Rowe, *Chem. and Ind.*, 1962, 92. [d] J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.*, 1963, 3371. [e] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

The direction of polarisation of the P–M–Cl group moment must be such that phosphorus is positive and chlorine negative. Evaluation of the charges on the phosphorus, metal, and chlorine atoms from the group moment is difficult. It is necessary to assign a moment to one or other of the bonds before one can calculate charges. On the basis of a point-charge model, and assuming that the M–Cl moment in *cis*-$[PtCl_2(PEt_3)_2]$ is 2 D and the balancing P–M moment is *ca.* 5—6 D, it follows that the phosphorus atom is positively charged and that both the chlorine and platinum atoms are negatively charged.[2] This assignment was successfully used by Chatt and his co-workers to determine configurations of a large number of complexes before n.m.r. spectroscopy became available, although the basis of the original assignment (*i.e.* from the moment and supposed shape of $[NiBr_3(PEt_3)_2]$)[3] is no longer valid.[4]

We can get some idea of the moment associated with a co-ordinate bond from the work of Phillips *et al.*[5] The dipole moments of $Me_3P{\rightarrow}BCl_3$ and $Ph_3P{\rightarrow}BCl_3$ are 7.03 and 7.0 D respectively, so that substituents on phosphorus have little influence on the dipole moment. The moment of triphenylphosphine is 1.39 D, and that of trimethylphosphine was estimated to be 1.2 D, so that the moment associated with the $P{\rightarrow}BCl_3$ part of the molecule is *ca.* 5.7 D. It is necessary to correct this for the moment of 'tetrahedral' BCl_3. The dipole moment of chloroform is 1.2 D. Assuming that the C–H bond moment is *ca.* 0.5 D with the carbon positive, then the CCl_3, and by inference the BCl_3, group moment must be *ca.* 1.7 D, and the P→B moment is *ca.* 4.0 D. If the P→Pt bond moment is of similar magnitude, we infer that the P–Pt bond is slightly more polar and in the opposite sense to the Cl–Pt bond.

More recently Carlson and Meek[6] discussed the polarity of bonds such as P→O, P→S, and P→B. The bond moments of P→O are of the order of 2.5—3.3 D, depending on the substituents on the phosphorus. In trimethylphosphine oxide the bond moment is 3.04 D and the total P→O charge separation is 0.43 electrons. In the corresponding P→S bond the charge separation is 0.3 e with a bond moment of 3.78 D. The group moment for $P{\rightarrow}BH_3$, derived from measurements[7] on $Me_3P{\rightarrow}BH_3$ and $MeH_2P{\rightarrow}BH_3$, is 3.69 D.[6] Assuming that the dipole moment of tetrahedral BH_3 is equal to that of CH_3 in CH_4, the moment of BH_3 is equivalent to that of a C–H bond, *i.e.* 0.4 D with boron positive. Hence the P→B bond moment is *ca.* 3.3 D. In this case extrapolation to P→Pt indicates that P→Pt and Pt–Cl bond moments are approximately equal.

The determination of the relative magnitudes of bond polarities is important because whether the charge on the metal atom is positive or negative depends on whether or not the P–M bond moment is greater than the M–Cl moment, the P–M and M–Cl bond lengths being approximately equal. In complexes with only highly electronegative ligand atoms, *e.g.* as in water, amines, or chloride, the metal is probably positively charged, but in complexes containing several good electron-donor ligands with somewhat electropositive atoms such as induce a strong inductive *trans* effect, *e.g.* tertiary phosphines, hydride, and methyl, and particularly where low-oxidation-state complexes are involved, the metal is probably negative.

The data in Table 1 allow us to make general inferences about charges carried by various groups. If we assign charges x and y to the phosphorus and chlorine atoms in *cis*-$[Pt(PEt_3)_2Cl_2]$, the charge on the platinum is $-2(x + y)$. If in some complexes $[MCl_3(PR_3)_3]$ (M = Ru, Os, Rh, Ir, Re, *etc.*; PR_3 = tertiary phosphine) the charges

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[1] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 225, 250.

[2] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1952, 273.

[3] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.

[4] D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 4920.

[5] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 1945, 146.

[6] R. R. Carlson and D. W. Meek, *Inorg. Chem.*, 1974, **13**, 1741.

[7] P. S. Bryan and R. L. Kuczinski, *Inorg. Chem.*, 1972, **11**, 553.

on the phosphorus and chlorine atoms are still x and y, the charge on the metal atom must be $-3(x + y)$. Hence, even in *mer*-[MCl$_3$(PR$_3$)$_3$] complexes where the dipole moment is equal to a single P–M–Cl group moment, one would expect the group moment to be different from that calculated for the P–M–Cl group in a similar square-planar complex because the charge on the metal atom is different. The fact that the P–M–Cl group moments cover only a short range of values implies that the charge on the metal must be *ca.* 0. If so, calculation shows that the charges on the phosphorus and chlorine atoms are *ca.* +0.3 and −0.3 e respectively. The charge on the metal in an uncharged complex is then *ca.* 0 and essentially independent of oxidation state, provided that equal numbers of tertiary phosphine and chloride ligands are attached.

Table 2 gives dipole moments of some metal hydrido-, carbonyl, and nitrosyl complexes. Also included are group moments, calculated on the basis that the P–M–Cl group moment is 6.8 D. Considering first the Cl–M–CO moments, it can be seen that where the group moment, due to axial symmetry of the complex, is equal to the measured dipole moment, Cl–M–CO has a group moment of 2—3 D. This implies that CO is a weak donor,[8] considerably poorer than a tertiary phosphine, and is probably actually withdrawing electronic charge, which accords with its behaviour in, say, [Ni(CO)$_4$].[9] Where the Cl–M–CO moment has to be inferred from the vector sum of other bond moments, the consistency vanishes. This is probably caused by the imbalance between the number of phosphine and chloride ligands on the metal so that the metal acquires, in these particular cases, a positive charge which invalidates the simple apportioning of bond moments. We also infer from the data in Table 2 that the nitrosyl ligand carries about the same charge as carbonyl, as confirmed by the very low moment of [Co(CO)$_3$(NO)] (≈0.4 D).[8] The dipole moment of *cis*-[PtCl$_2$(PF$_3$)$_2$] (4.4 D) indicates that phosphorus trifluoride is equally electron withdrawing.[10] In the hydride complexes in Table 2 the hydride ligand appears to be slightly positive. This is an expression of its strong inductive *trans* effect [11] which renders the *trans* chloride more negative than is usual and in fact hydride is probably only slightly negative.

At present, without independent determination of a single charge or bond moment, this analysis cannot be carried further. However, the above inferences concerning atomic charges are consistent with the *X*-p.e. spectroscopic data below.

X-*P.e. Measurements*.—The binding energy of an electron in a metal atom is often held to be characteristic of the oxidation state of the metal ion, but this can never be so except in comparison of closely analogous compounds. At its simplest, the binding energy of an electron of a metal ion in a complex is a measure of the electric potential in the electron shell containing the electrons under study. The oxidation state is the num-

TABLE 2

Some group moments (D) involving Cl, CO, and NO ligands

Complex	Observed dipole moment	Group moment	Relation of dipole and group moments
trans-[Rh(CO)Cl(PEt$_2$Ph)$_2$]	2.4 [a]	Cl–M–CO 2.4	Equivalent
trans-[Ir(CO)Cl(PEt$_2$Ph)$_2$]	2.1 [b]	Cl–M–CO 2.1	Equivalent
trans-[Ir(CO)Cl(PPh$_3$)$_2$]	2.1 [b]	Cl–M–CO 2.1	Equivalent
trans-[Re(CO)Cl(PMe$_2$Ph)$_4$]	2.0 [21]	Cl–M–CO 2.0	Equivalent
mer-trans-[Rh(CO)Cl$_3$(PEt$_2$Ph)$_2$]	3.6 [a]	Cl–M–CO 3.6	Equivalent
mer-trans-[Ir(CO)Cl$_3$(PEt$_3$)$_2$]	2.8 [b]	Cl–M–CO 2.8	Equivalent
mer-cis-[Ru(CO)Cl$_2$(PEt$_2$Ph)$_3$]	7.5 [c]	Cl–M–CO 4.7	Inferred
cis-cis-trans-[Os(CO)$_2$Cl$_2$(PEt$_2$Ph)$_2$]	4.3 [d]	Cl–M–CO 3.0	Inferred
fac-cis-[Ir(CO)Cl$_3$(PBu$^n{}_3$)$_2$]	12.4 [b]	Cl–M–CO 8.1	Inferred
cis-[Pt(CO)Cl$_2$(PPr$^n{}_3$)]	10.2 [e]	Cl–M–CO 6.6	Inferred
cis-[Pt(CO)Cl$_2$(PEt$_3$)]	10.0 [e]	Cl–M–CO 6.5	Inferred
cis-[Pt(CO)$_2$Cl$_2$]	4.7 [10]	Cl–M–CO 3.4	Inferred
trans-[PtH(Cl)(PEt$_3$)$_2$]	4.2 [f]	Cl–M–H 4.2	Equivalent
trans-[PtH(Cl)(PPh$_3$)$_2$]	4.4 [f]	Cl–M–H 4.4	Equivalent
trans-[RuH(Cl)(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]	4.8 [g]	Cl–M–H 4.8	Equivalent
trans-[OsH(Cl)(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]	5.1 [g]	Cl–M–H 5.1	Equivalent
trans-[FeH(Cl)(Et$_2$PCH$_2$CH$_2$PEt$_2$)$_2$]	4.3 [h]	Cl–M–H 4.3	Equivalent
mer-cis-[Ir(CO)Cl$_3$(PEt$_3$)$_2$]	9.5 [b]	P–M–CO 6.8	Inferred
[W(CO)$_5$(PH$_3$)]	4.1 [i]	P–M–CO 4.1	Equivalent
[Cr(CO)$_5$(PPh$_3$)]	5.5 [j]	P–M–CO 5.5	Equivalent
[Fe(CO)$_4$(PPh$_3$)]	5.1 [k]	P–M–CO 5.1	Equivalent
mer-trans-[Ru(NO)Cl$_3$(PEt$_2$)$_2$]	2.8 [l]	Cl–M–NO 2.8	Equivalent
mer-cis-[Re(NO)Cl$_2$(PEt$_2$Ph)$_3$]	6.3 [36]	Cl–M–NO 0	Inferred

[a] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437. [b] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1625; *J. Chem. Soc.* (*A*), 1967, 604. [c] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466. [d] W. Hieber, V. Frey, and P. John, *Chem. Ber.*, 1967, **100**, 1961. [e] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662. [f] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075. [g] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605. [h] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 5507. [i] W. Bathelt, quoted by P. John, *Chem. Ber.*, 1970, **103**, 2178. [j] H. Tengler, quoted by P. John, *Chem. Ber.*, 1970, **103**, 2178. [k] W. Manchot and J. König, *Ber.*, 1924, **57**, 2130. [l] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1811.

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[8] E. Weiss, *Z. anorg. Chem.*, 1956, **287**, 223.

[9] M. Barber, J. A. Connor, I. H. Hillier, and V. R. Saunders, *Chem. Comm.*, 1971, 682.

[10] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1951, 3061.

[11] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

ber of electrons to be added to reduce (or removed to oxidise) the complex to the metallic element and its free ligands (anions and uncharged molecules) in a real or hypothetical redox reaction.

There is no reason for any direct relation between the two, but generally it is expected that the more electrons are needed for the reduction (*i.e.* the higher the oxidation state) the greater the chance that the metal will carry a more positive charge. It is now clear that the binding energy can vary between wide limits in any given oxidation state of the metal, depending on the ligands. Tolman *et al.*[12] have shown that the measured binding energies of a series of nickel(II) complexes span a range with lower values which are also typical of some Ni^0 complexes. The use of binding energies in an attempt to determine oxidation numbers, except against an extensive background of empirical knowledge, can be very misleading.

TABLE 3

X-p.e. spectroscopic and electrochemical data for some rhenium complexes

Complex	Formal oxid-ation state	Ob-served metal po-tential [a]	Binding energies (eV)					E' [b]/mV	
			Re($4f_{\frac{5}{2}} + 4f_{\frac{7}{2}}$)	Cl($2p_{\frac{3}{2}}$)	P($2p_{\frac{3}{2}}$)	N($1s$)	O($1s$)	Reduction	Oxidation
[ReCl$_2$(PMe$_2$Ph)$_4$] (I)	II	2.0	43.0, 40.7	198.4	131.3				−508
[ReCl$_3$(PMe$_2$Ph)$_3$] (II)	III	3.0	44.0, 42.0	195.8	131.4			−890 [c]	+711
[ReCl$_4$(PMe$_2$Ph)$_2$] (III)	IV	4.0	46.3, 43.8	199.4	132.1			−167	
[ReCl$_2$(N)(PEtPh$_2$)$_2$] (IV)	V	3.4	45.2, 42.9	199.2	132.0	398.8			+588
[ReCl$_2$(N)(PMe$_2$Ph)$_3$] (V)	V	2.2	42.9, 40.9	198.2	131.6	398.0		−970 [c]	>1 030 [d]
cis-[ReCl$_3$(NMe)(PMe$_2$Ph)$_2$] (VI)	V	3.8	45.5, 43.4	198.8	131.7	399.8		*ca.* −1 400 [c]	+1 030 [c]
trans-[ReCl$_3$(NMe)(PMe$_2$Ph)$_2$] (VII)	V							*ca.* −1 400 [c]	+1 030 [c]
[ReCl$_3$(NPh)(PEtPh$_2$)$_2$] (VIII)	V	3.8	45.4, 43.5	198.9	131.9	399.5			
[ReCl(N$_2$)(PMe$_2$Ph)$_4$] (IX)	I	1.9	42.9, 40.5	198.7	131.8	400.1 398.4			+48
[ReBr(N$_2$)(PMe$_2$Ph)$_4$] (X)	I	2.2	42.8, 40.9		131.2	400.1 398.5			
[ReBr(N$_2$)(py)(PMe$_2$Ph)$_3$] (XI)	I	2.2	43.0, 41.0		131.2	399.6 398.0			−53
[ReCl(N$_2$)(py)(PMe$_2$Ph)$_3$] (XII)	I	2.2	43.0, 41.0		131.3	399.8 398.3			−85
[ReCl(N$_2$)(py)(PMePh$_2$)$_3$] (XIII)	I	2.3	43.1, 41.1		131.4	399.9 398.2			+15
[ReCl(N$_2$)(CO)(PMe$_2$Ph)$_3$] (XIV)	I		Decomposes in X-ray beam, losing N$_2$						+567
[ReCl(N$_2$)(CO)$_2$(PPh$_3$)$_2$] (XV)	I		Decomposes in X-ray beam, losing N$_2$						+910 [c]
[Re(N$_2$)(PMe$_2$Ph)$_3$(S$_2$CNEt$_2$)] (XVI)	I	1.4	41.8, 39.8		131.0	399.8 [e]			−260 (−270)
[ReCl(N$_2$)(PMe$_2$Ph)$_4$][FeCl$_4$] (XVII)	II	3.1	44.4,42.2	199.2	131.9	400.1		+48	
[ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (XVIII)	I	1.6	42.4, 40.0	197.5	131.0	400.9 398.8			+121
[ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][FeCl$_4$] (XIX)	II	2.7	43.6, 41.7	198.6	131.2	400.3		+121	
[(PhMe$_2$P)$_4$ClRe(N$_2$)MoCl$_4$(OMe)] (XX)	I	2.3	43.3,41.2	198.6	131.4	398.6			+200
[ReCl(CO)(PMe$_2$Ph)$_4$] (XXI)	I	1.9	42.9, 40.5	198.2	131.4		532.4		+410
[ReCl(CO)(PMe$_2$Ph)$_4$][FeCl$_4$] (XXII)	II	2.9	44.4, 42.1	199.0	131.5		532.4	+410	
[ReCl(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (XXIII)	I	1.9	42.6, 40.4	198.2	131.2		532.4		
[ReCl(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]I$_3$ (XXIV)	II	2.2	43.1, 40.9	198.1	131.2		532.5		
[ReCl$_2$(NO)(PMePh$_2$)$_2$] (XXV)	II	3.9	45.6, 43.6		131.8	401.2	532.6	−500 (−510)	+865 [c]
[ReCl$_2$(NO)(PMePh$_2$)$_3$] (XXVI)	II	3.2	44.8, 42.5			401.3	532.6		+932
[ReCl$_2$(NO)(CO)(PMePh$_2$)$_2$] (XXVII)	II	3.7	45.5, 43.3		131.8	401.6	532.3 [e]		
[ReCl$_3$(NO)(PMePh$_2$)$_2$] (XXVIII)	III	3.9	45.9, 43.8			401.5	533.0	−52	
Cs[ReCl$_3$(NO)(PMePh$_2$)$_2$] (XXIX)	II	3.1	44.4, 42.4	198.2	131.5	401.2	532.0		−52
[ReCl$_4$(NO)(PMePh$_2$)$_2$] (XXX)	IV	3.9	45.8, 43.8		131.9	400.9	532.0	−173	
[ReH$_5$(PMe$_2$Ph)$_3$] (XXXI)	V	1.9	42.9, 40.5		131.4				

[a] See text for definition. [b] Figures in parentheses were measured at a dropping mercury electrode. [c] Irreversible. [d] Obscured by solvent discharge. [e] Broad signal, more than one kind of oxygen or nitrogen involved.

The binding energy is a measure of the potential field in which the expelled photoelectron was moving, but its measurement is complicated by secondary effects due to crystal fields, excited states, *etc.* We sought to minimise these secondary effects by comparing compounds of similar structure, where possible with very small differences, *e.g.* complexes which differ in only one ligand. We have chosen as references three arbitrary standards, complexes (I)—(III) in Table 3. These were chosen because we are concerned in the main with chloro-(tertiary phosphine) complexes. Had we chosen a different analogous series, *e.g.* [ReCl$_n$(NR$_3$)$_{6-n}$] or [ReCl$_n$(CO)$_{6-n}$], if they had existed, we would have found a different quantitative relation between oxidation number and binding energy.

The ($4f_{\frac{7}{2}}$) electron binding energies of the 'standard' complexes [ReCl$_2$(PMe$_2$Ph)$_4$], (I), [ReCl$_3$(PMe$_2$Ph)$_3$], (II), and [ReCl$_4$(PMe$_2$Ph)$_2$], (III), are used as characteristic of the formal oxidation states II, III, and IV, respectively, and are plotted against the formal oxidation states to determine the position of the line shown in Figure 1. One would not necessarily expect a linear relation between formal oxidation state and electron binding energy

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[12] C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, 1973, **12**, 2770.

in such a series of complexes,[13] but empirically it is linear to within experimental error over the short range available. In our complexes replacement of a ligating chlorine atom (not a chloride ion) by a tertiary phosphine ligand lowers the $(4f_{\frac{7}{2}})$ electron binding energy by *ca.* 1.5 eV.* The relation would allow us to infer 'fractional' oxidation states relative to our standard but, because oxidation state is determined by formal electron oxidation or reduction steps which require an integral value to be assigned, this is not satisfactory. We therefore used Figure 1 to determine, by interpolation, not fractional oxidation states but the potential corresponding to the Re $(4f_{\frac{7}{2}})$ state in the complexes under investigation relative to our standards. This observed metal potential (o.m.p.) is measured in oxidation-state units on our arbitrary scale and can have non-integral values. The o.m.p. is shown for all complexes in Table 3 and also for selected complexes in Figure 1. At best our binding energies can be determined to ±0.2 eV and it is not possible to ascribe significance to differences in o.m.p. of less than *ca.* 0.3 and in most cases to less than 0.4.

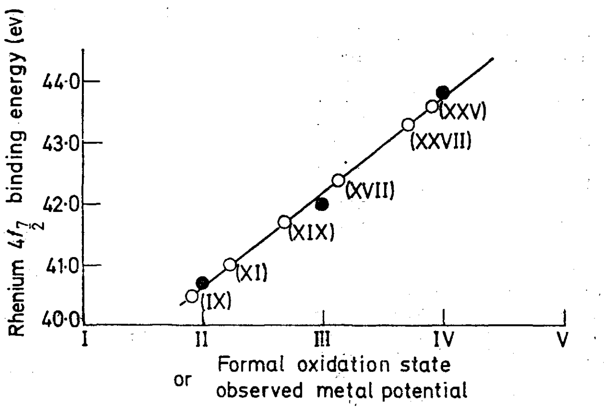

FIGURE 1 Determination of observed metal potential (o.m.p.) for selected complexes from Table 3 (○). (●), Standard complexes

Nitrosyl Complexes of Rhenium.—These comprise complexes (XXV)—(XXX) in Table 3. The N(1*s*) electron binding energies are within the range 400.9—401.6 eV, which suggests that, on the basis of any of the several correlations between binding energy and charge proposed for nitrogen, the nitrogen atoms are neutral or slightly negatively charged. The binding energies lie within the range of values derived by Finn and Jolly for linear M–N–O systems.[14] The angle Re–N–O is 180° in (XXVI).[15] The O(1*s*) binding energies are also indicative of negative charges, so that the N–O ligand as a whole appears to carry a negative charge, irrespective of its mode of binding and even when it uses three electrons in bonding (so-called NO^+). This agrees with the report of Beck [16] who inferred that 'NO^+' is more negative than 'NO^-', without excluding the possibility that both might be, in absolute terms, positive. The $Cl(2p_{\frac{3}{2}})$ and $P(2p_{\frac{3}{2}})$ electron binding energies are relatively invariant in our complexes and we make no inference concerning their magnitudes, but the Re(4*f*) energies are much more informative and are consistent with our deductions from dipole-moment data concerning relative atomic charges. In addition $P(2p_{\frac{3}{2}})$ probably does not change much on co-ordination.[12]

The o.m.p. of rhenium in the complex $[ReCl_2(NO)(PMePh_2)_3]$, (XXVI), is 3.2 and hence NO is about as electron withdrawing as the chlorine atom it formally replaces in $[ReCl_3(PMePh_2)_3]$, (II). This is also true of NO in the higher-oxidation-state complexes (XXVIII) as compared with (III). It is to be noted that the formal oxidation state of rhenium in (XXVI) is II, because NO is an uncharged ligand. Removal of a phosphine from (XXVI) to give $[ReCl_2(NO)(PMePh_2)_2]$, (XXV), raises the o.m.p. to 3.9. This means that addition or removal of a tertiary phosphine ligand is equivalent to reduction or oxidation of rhenium by three quarters of a unit. In binding energies this constitutes a difference of *ca.* 1 eV. Evidently the phosphine is a good electron donor. Addition of carbon monoxide to (XXV) to yield $[ReCl_2(NO)(CO)(PMePh_2)_2]$, (XXVII), causes the o.m.p. to decrease to 3.7, which is unchanged within the prescribed limit of error. We infer that carbonyl in this complex is approximately neutral, perhaps slightly electron donating, and certainly less electron withdrawing than nitrosyl.

Addition of a chlorine atom to (XXV) to give $[ReCl_3(NO)(PMePh_2)_2]$, (XXVIII), raises the formal oxidation state by one unit but leaves the o.m.p. unchanged. Allowing for experimental error, we infer that addition of a chlorine atom raises the binding energy by less than *ca.* 0.5 eV in this case. Since removal of a phosphine ligand causes an increase of 1.0 ± 0.3 eV, the 1.5 eV change in binding energy per unit change in oxidation state observed in our standards can be apportioned 1.0 eV to removal of a phosphine and 0.5 eV to addition of a chlorine atom. This suggests that phosphorus carries a greater positive charge than the chlorine atom does negative charge.

In contrast to addition of a chlorine atom, addition of a chloride ion to (XXV) to give $[ReCl_3(NO)(PMePh_2)_2]^-$ reduces the binding energy by *ca.* 1 eV and the o.m.p. from 3.9 to 3.1 as observed in the caesium salt (XXIX). This complex may not be directly comparable to the others because it is a salt and the Madelung effects will be different. However, the observation agrees with the intuitive prediction that Cl^- should be a much better electron donor than a chlorine atom. Finally in this group, the seven-co-ordinate nitrosyl complex $[ReCl_4(NO)(PMePh_2)_2]$, (XXX), has an o.m.p. of 3.9. On the basis that addition of NO to (III) is approximately equivalent to addition of a chlorine atom, conversion of (III) into (XXX) should occur with only a small with-

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* 1 eV ≈ 1.60×10^{-19} J.

[13] G. J. Leigh, *Inorg. Chim. Acta*, 1975, **14**, 135.

[14] P. Finn and W. L. Jolly, *Inorg. Chem.*, 1972, **11**, 895.

[15] K. W. Muir, L. Manojlovic-Muir, and R. Herak, unpublished work.

[16] F. Holsboer, W. Beck, and H. D. Bartunick, *J.C.S. Dalton*, 1973, 1828.

drawal of charge from the rhenium atom (see preceding paragraph) so that (III) and (XXX) should have the same binding energies to within experimental error (±0.3 eV).

Extrapolation of the inferred ligand properties outside of phosphine complexes and II—IV rhenium oxidation states should be treated with caution, *e.g.* the *X*-p.e. spectroscopic data for the carbonyl complexes (XXI)—(XXIV) discussed below indicate that, in compounds of low-oxidation-state metals, carbon monoxide is electron withdrawing. In competition with nitrosyl, however, carbonyl is the weaker acceptor, and is much more nearly neutral [compare (XXVII) and (XXV) which have similar o.m.p.]. Nevertheless we feel that our generalisations concerning tertiary phosphine, chlorine-atom, and chloride-ion ligands are more widely applicable than those relating to carbonyl and nitrosyl because the phosphorus and chlorine are less polarisable than those small unsaturated ligands.

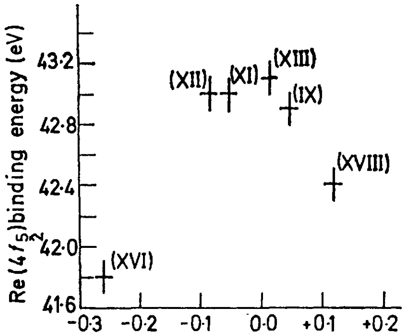

FIGURE 2 Relation of rhenium $4f_{\frac{5}{2}}$ binding energies and redox potentials for some dinitrogen complexes

Dinitrogen and Carbonyl Complexes of Rhenium.—All the rhenium(I) dinitrogen complexes (IX)—(XVI) and (XVIII) contain dipolar dinitrogen, the separation of N(1*s*) binding energies being *ca.* 1.7 eV. Similar observations have been reported by Finn and Jolly,[17] Nefedov *et al.*,[18] and Folkesson.[19] In the dithiocarbamate complex (XVI) the N(1*s*) band is broad and symmetric with no resolution. The pyridine complexes (XI)—(XIII) show two N(1*s*) bands, intensity ratio 2 : 1, the more intense being at higher binding energy. Both nitrogen atoms of the dinitrogen ligand appear to be absolutely negatively charged on the basis of binding energy–charge correlations, and this is further supported by the rhenium binding energies. Thus, $[ReCl(N_2)(PMe_2Ph)_4]$ has an o.m.p. of 1.9, although the formal oxidation state is I. Hence, dinitrogen is about as electron withdrawing as chlorine in the Re^I complexes. In the analogous Re^{II} complexes (XVII) and (XIX) the polarity of the dinitrogen is lower and so is its nett negative charge. The N(1*s*) binding energies are close to those of the more positive nitrogen in the Re^I dinitrogen complexes, but there is no way of labelling the nitrogen atoms to determine which nitrogen atom is the more positive. The o.m.p. of rhenium in $[ReCl(N_2)(PMePh_2)_4][FeCl_4]$ is 3.1, again consistent with a negative electron-withdrawing dinitrogen (approximately equal to chlorine) but the inference is uncertain due to the different Madelung effect in the salt.

We had hoped to compare the electron-withdrawing powers of dinitrogen and carbonyl by a study of the complexes (XIV) and (XV), but these decompose in the *X*-ray beam losing dinitrogen but retaining carbonyl which is apparently more strongly bound. The chemistry of complexes (XXI)—(XXIV) indicates that carbonyl is more electron withdrawing than dinitrogen, *e.g.* the rhenium(I) carbonyls are less easily oxidised than their dinitrogen analogues (compare the relevant redox potentials) and the rhenium(II) carbonyls are more easily reduced.[20] The carbonyl complexes (XXI)—(XXIV) have o.m.p.s virtually identical with those of their dinitrogen analogues, so that on the grounds of competition and comparison the electron-withdrawing abilities of nitrosyl, carbonyl, and dinitrogen are in the order $NO > CO = N_2$. However, since their polarisabilities will be different, this order could possibly change in complexes with other metal ions or with other co-ligands. Comparison of dipole moments of pairs of analogous complexes, *e.g.* $[Ni(CO)_4]$(0.0) and $[Co(CO)_3(NO)]$, (0.43),[8] $[ReCl(N_2)(PMe_2Ph)_4]$, (1.25) and $[ReCl(CO)(PMe_2Ph)_4]$, (2.0 D),[21] confirms that the charges carried by these three ligands are of similar magnitude, probably small, with the dinitrogen slightly more negatively charged than carbonyl.[19]

The complex $[(PhMe_2P)_4ClRe(N_2)MoCl_4(OMe)]$, (XX), possesses a somewhat long dinitrogen molecule (1.18 Å) bridging linearly between the rhenium and molybdenum atoms.[22] The rhenium has o.m.p. 2.3 and is perhaps slightly oxidised compared with (IX). The dinitrogen is no longer dipolar and is overall more negative than in (IX), presumably indicating electron withdrawal from both rhenium and molybdenum although this seems unlikely.

Complexes with Other Nitrogen Ligands.—The complexes (IV)—(VIII) are related, but we had to change the tertiary phosphines in order to obtain satisfactory complexes. Thus the appropriate homologue of (IV) would be $[ReCl_2N(PEtPh_2)_3]$, but this loses a phosphine ligand on *X*-irradiation in high vacuum to give $[ReCl_2N(PEtPh_2)_2]$, (IV), so we used the more stable $[ReCl_2N(PMe_2Ph)_3]$, (V).

The complex $[ReCl_2N(PMe_2Ph)_3]$, (V), has an o.m.p. of 2.2, whereas the formal oxidation state of the rhenium is V. Comparison with complex (II) appears to indicate that the nitrogen atom, as a ligand, is considerably less electron withdrawing than chlorine, and comparison with (I) that it is nearly as electron releasing as a tertiary

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[17] P. Finn and W. L. Jolly, *Inorg. Chem.*, 1972, **11**, 1434.

[18] V. I. Nefedov, M. A. Porai-Koshits, I. A. Zakharova, and M. E. Dyatkina, *Doklady Akad. Nauk S.S.S.R.*, 1972, **202**, 605.

[19] B. Folkesson, *Acta Chem. Scand.*, 1973, **27**, 1441.

[20] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

[21] J. Chatt, R. H. Crabtree, E. A. Jeffery, and R. L. Richards, *J.C.S. Dalton*, 1973, 1167.

[22] M. Mercer, *J.C.S. Dalton*, 1974, 1637.

phosphine which is unlikely. However, the N(1*s*) binding energy is low [as are Cl($2p_{\frac{3}{2}}$) and P($2p_{\frac{3}{2}}$)] so that there appears to be negative charge on all the ligands in this molecule as well as on the metal. This contradiction may be an artefact resulting from charging of the complex during irradiation, but more probably it is explained by some peculiarity arising from the bonding of the nitrogen atom which we do not understand. It seems that simple charge-binding energy correlations are not valid for this particular group of complexes. Comparison of [$ReCl_2N(PEtPh_2)_2$], (IV), with (V) shows 'oxidation' (o.m.p. increases from 2.2 to 3.4) characteristic of removal of a tertiary phosphine, so that the binding energies of both nitrido-complexes are self consistent which would be unlikely if charging were occurring. Comparison of (IV) and (V) with (XXV) and (XXVI), respectively, suggests that the nitride ligand carries rather less negative charge than the nitrosyl and considerably less than that corresponding to its formal charge (3−) otherwise the o.m.p. would approach 5. The alkylimido- and arylimido-complexes (VI) and (VIII) have essentially similar electronic distributions and the NPh and NMe ligands in them seem similar to chlorine in their electron-withdrawing properties [*cf.* (III)]. Because of uncertainties in the interpretation of *X*-p.e. spectroscopic data in this group of complexes these conclusions must be regarded as tentative.

Hydrido-complex.—Hydride ion is a strongly σ-electron-releasing anionic ligand which exerts a very strong inductive *trans* influence. In [$ReH_5(PMe_2Ph)_3$], (XXXI), the rhenium has an o.m.p. of 1.9 which is very much less than the formal oxidation state of V and suggests that the hydrogen carries little charge. The metal accommodates a considerable amount of the hydride anionic charge, and is less positive than in [$ReCl_3(PMe_2Ph)_3$], (II), although there is no indication of this in the P($2p_{\frac{3}{2}}$) energies, which, as noted above, are relatively invariant. Analogous molybdenum, tungsten, and osmium hydrido-complexes show similar low o.m.p.[13] This small charge separation may account for the great number of hydride ligands which can be carried by metals such as rhenium. These contain sufficient vacant orbitals to bond up to nine ligands and need a great number of hydrogen ligands to accommodate the negative charge from the metal in, for example, [ReH_9]$^{2-}$ or [$ReH_5(PR_3)_3$].

Redox Studies.—The electrochemical measurements are also summarised in Table 3. For the majority of complexes studied the parameter *E′* is defined as the formal potential (relative to the saturated calomel electrode, s.c.e.) of the reversible redox couples. The *E′* values were equated to half-wave potentials as measured by cyclic voltammetry or polarography under the experimental conditions described elsewhere.[23] In some cases one member of the couple was chemically labile and underwent a substitution reaction subsequent to the charge-transfer step. The rates of these substitution reactions were sufficiently slow to cause only a small shift (<50 mV) in *E′* from the true reversible value. Also listed in Table 3 are six electrode reactions that were totally irreversible and *E′* values are estimated from either cyclic voltammograms at slow scan rates (*V* 30 mV s^{-1}) of polarographic half-wave potentials.

The electrochemical experiments measure the potential of a redox orbital. These, being the occupied molecular orbitals of highest energy (h.o.m.o.) or the vacant orbitals of lowest energy (l.e.m.o.), are of *d*, *p*, or π character, readily polarisable, and sensitive to solvation effects. However, by choice of very similar complexes, variations in such effects were minimised.

It has been shown in six-co-ordinate complexes such as we have investigated that the redox orbital (h.o.m.o. or l.e.m.o.) is composed predominantly of the metal atomic orbitals with only a small contribution from the ligand orbitals.[24] Because of its polarisability, the redox orbital should be highly sensitive to the absolute charge on the metal and it is important to see how far our redox measurements reflect this charge. Since *X*-p.e. spectroscopy gives the most direct indication of the latter, we plotted the binding energy against *E′*. For a correlation to be observed one might expect *a priori* at least the following conditions to be fulfilled: (*a*) the Madelung effects must be relatively invariant as they probably are (see above); (*b*) the rate of electron transfer to or from the electrode be rapid and not the rate-determining step; (*c*) differences between the solvation energies of the complexes must be small and conditions and complexes have been chosen to minimise them as far as possible; and (*d*) the metal contribution to the redox orbital must be constant. Although the plot shows general agreement that the higher the binding energy the higher *E′*, there is no detailed correlation. Apparently there are some important perturbing factors, and, in our opinion, the most important is d_π–p_π bonding in its effect on (*d*). These π-type interactions are more important than inductive electronic effects in stabilising unusual oxidation states of transition metals in their complexes because they involve directly the outer *d* shell which contains the redox orbitals.[25]

π-Type bonding influences oxidation or reduction potentials by an essentially electrostatic mechanism. Perhaps the most striking demonstration of this is Gel'man and Ryabchikov's [26] comparison of the oxidation of the salts [NH_4][$PtCl_3(NH_3)$] (*a*), K[$PtCl_3(C_2H_4)$] (*b*), and [NH_4][$PtCl_5(NH_3)$] (*c*) which they titrated with 4.1N-potassium permanganate in dilute sulphuric acid solution at room temperature. Only the platinum(II) complex (*a*) was oxidised with an initial potential of 520 mV on a bright platinum electrode against the s.c.e. The Pt^{II}, (*b*), and the Pt^{IV} complex, (*c*), were more resistant to

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[23] C. M. Elson, *J.C.S. Dalton*, following paper.

[24] F. A. Cotton, 'Chemical Applications of Group Theory,' Interscience, New York, 1964, p. 225; Yu. G. Borodko and A. E. Shilov, *Russ. Chem. Rev.*, 1969, **38**, 355; P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, **87**, 3340.

[25] J. Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 516.

[26] A. D. Gel'man and D. I. Ryabchikov, *Compt. Rend. Acad. Sci. U.R.S.S.*, 1941, **83**, 462.

oxidation, with initial potentials of 650 and 660 mV respectively. The olefin, allowing for rotation, can only interact directly with two of the three 'non-bonding' *d* orbitals, but it lowers the energy of all three to such an extent that the platinum(II) olefin complex behaves like a platinum(IV) ammine. It is difficult to believe that the olefin removes total charge from the metal as effectively as the two much more electronegative chlorine atoms. Evidently the oxidation potential is much more sensitive to mesomeric electronic effects (withdrawal by back bonding into the olefin) than to inductive effects (electron withdrawal in the σ bond to the chlorine).

Bearing these observations in mind, one can make some useful comparisons between similar ligands based on our electrochemical measurements. The redox potentials are capable of much more accurate measurement and are more sensitive to ligand changes than either dipole moment or *X*-p.e. spectroscopic measurements, and can be used to observe differences not apparent through those methods. Complexes (I)—(III) were examined to determine the behaviour of our standard complexes containing rhenium in oxidation states II, III, and IV respectively. It is to be noted that the first could not be reduced nor the last oxidised in the solvent system used. The rhenium(I) dinitrogen complexes (IX)—(XIII) are non-reducible but easily oxidised, having oxidation potentials of *ca.* 0 mV. Their resistance to oxidation is approximately midway between that of our standard rhenium complexes (I) and (II), and rather greater than would be expected from their o.m.p.s of 1.9—2.3, presumably due to π bonding to the dinitrogen. The carbonyl complex (XXI) (E' +410 mV) is more resistant to oxidation than its dinitrogen analogue (IX) (E' +48 mV) and its oxidation potential approaches that of (II), of o.m.p. 3, but its o.m.p. is only 1.9.

The above result indicates that carbon monoxide is much more effective than dinitrogen in withdrawing electronic charge from the metal and so stabilising the redox orbital. This is consistent with completely independent analyses based on Mössbauer[27] and i.r. spectroscopy.[28,29] Nevertheless both the dipole moment and *X*-p.e. spectroscopic results indicate that dinitrogen and carbon monoxide carry approximately the same charge. Evidently carbonyl owes its ability to raise oxidation potentials to its greater capacity for back bonding, *i.e.* a mesomeric electron withdrawal, whereas dinitrogen is more effective in its inductive withholding of electronic charge.

The effect of replacing dinitrogen or carbonyl from the Re^{I} complexes (IX) or (XXI) respectively by a chlorine atom is to give (I), a Re^{II} complex. Despite the fact that a formal oxidation has occurred this Re^{II} complex is the most easily oxidised in Table 3 (E' −508 mV). Nevertheless, (I), (IX), and (XXI) all have o.m.p.s of *ca.* 2. The *X*-p.e. studies indicate that addition of a chlorine atom to a complex has approximately the same effect on the metal charge as addition of a dinitrogen or carbonyl ligand. Nevertheless, this electrochemical measurement shows that the chlorine atom as a ligand is much less effective in decreasing the energy of the h.o.m.o. than either dinitrogen or carbonyl. These results can be explained on the basis that the electron-withdrawing capacity of dinitrogen and carbonyl arises substantially from d_π–π^* interaction whereas that of chlorine is inductive. Indeed any d_π–p_π bonding between the metal and chlorine atoms would take place between filled orbitals, so raising the h.o.m.o. energy and cancelling to some extent the effect of the inductive withdrawal. It is evident that in making comparisons of redox potentials one must use complexes containing closely similar ligands, and that except where π-type bonding between metal and ligand is essentially absent the difference between the π-bonding capacities of the ligands is the predominant factor in determining redox potentials. In these terms the following comparisons may be meaningful.

The two ligands producing the greatest change in oxidation potentials on substitution for chloride and/or phosphine are carbon monoxide, which is a strong π-electron acceptor, and diethyldithiocarbamate which is a strong π-electron donor. Replacement of a tertiary phosphine from (IX) by carbon monoxide to give (XIV) produces a shift of *ca.* +500 mV and replacement of the second tertiary phosphine molecule to give (XV) gives a further change of +350 mV, producing a Re^{I} complex which is more difficult to oxidise than our standard Re^{III} complex, (II). On the other hand, replacement of tertiary phosphine and chloride ion from (IX) by $Et_2NCS_2^-$ to give (XVI) lowers the oxidation potential by *ca.* 300 mV despite the fact that the sum of the electronegativity of the two sulphur atoms is equal to that of the atoms displaced. The dithiocarbamate group thus appears to be much more strongly electron releasing than (Cl^- + PMe_2Ph) as measured by both *X*-p.e. spectroscopy and the oxidation potential. Doubtless its strong electron-releasing character is associated with its tendency to the zwitterion form $Et_2\overset{+}{N}$–CS_2^{2-} in its complexes, as well as in the presence of somewhat readily polarisable filled *d* orbitals on the sulphur which by *d*-interaction would also raise the energy of the h.o.m.o.

Nitrosyl Ligands.—The six-co-ordinate nitrosyl complexes available for comparison with the standards are (XXVI), (XXVIII), and (XXIX). The first, $[ReCl_2(NO)(PMe_2Ph)_3]$ (XXVI), is more difficult to oxidise by *ca.* 200 mV than its chloro-analogue $[ReCl_3(PMe_2Ph)_3]$, (II), and it cannot be reduced because, unlike (II), it has no vacancy in the *d* shell. The second complex $[ReCl_3(NO)(PMe_2Ph)_2]$, (XXVIII), cannot be oxidised in the solvent system used, nor can its chloro-analogue $[ReCl_4(PMe_2Ph)_2]$, (III), but it can be reduced at −52 mV, *i.e.* at a potential 116 mV higher than its chloro-analogue. In both cases the nitrosyl group is more electron-withdrawing than the chlorine atom, in agreement with the

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[27] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mayo, and B. E. Prater, *J. Amer. Chem. Soc.*, 1972, **94**, 2847.

[28] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

[29] D. J. Darensbourg, *Inorg. Chem.*, 1971, **11**, 2399.

X-p.e. spectroscopic results. Both NO and Cl are odd-electron ligands with ligand atoms of about equal electronegativity but the effect of the nitrosyl group is probably enhanced by back bonding, especially in the lower-oxidation-state complex (XXVI).

We can also investigate replacement of a nitrosyl group by a tertiary phosphine by comparing (XXVI) with (I). This produces the enormous fall of 1 440 mV in oxidation potential. However, replacement of the nitrosyl group from (XXVIII) by a tertiary phosphine to produce (II) produces the smaller change of -838 mV in E' for the reduction steps. This again emphasises the strongly electron-withdrawing character of the nitrosyl relative to the tertiary phosphine ligands and indicates that back bonding to nitrosyl is much weaker in the higher-oxidation-state complex (XXVIII) than in (XXVI). Back bonding to phosphorus is apparently relatively unimportant in all these complexes.

Nitrido-, Phenylimido-, and Methylimido-ligands.—These three ligands are all attached by formal multiple bonds to the metal. They obviously therefore interact strongly with d orbitals not involved in σ bonding and comparison of the oxidation potentials of their complexes (V), (VI), and (VII) with those of our standards is of uncertain validity. The most obvious effect of these three multiply bonded ligands is to increase the difference between the energies of the l.e.m.o. and h.o.m.o. The splitting in the case of the nitrido-complex (V) is greater than 2 000 mV and for the two methylimido-complexes (VI) and (VII) is 2 430 mV. These formally Re^V complexes are markedly stabilised against reduction. They are all much more difficult to reduce than the standard complexes which are derived from them by replacing the nitrogen-containing ligand N⁝ or RN⁚ by a chlorine atom, despite the fact that the chloro-complex thus derived has a much lower formal oxidation state.

The enormous splitting between the l.e.m.o. and h.o.m.o. levels by these nitrogen ligands indicates that the d shell of the metal atom has been perturbed considerably by their presence, and it is doubtful whether any valid conclusions can be drawn concerning the charge carried by those ligands from a comparison with the oxidation or reduction potential of our standard complexes. All ligands multiply bonded to the metal must produce perturbations of this type but perhaps not so extreme. This casts considerable doubt on the value of the electrochemical method for determination of relative charge on the central metal atom in complexes other than those of exactly analogous electronic and steric structures.

Conclusions.—There is no method of determining the absolute charge on the metal and ligating atoms in a complex. Dipole-moment measurements, electron binding energies, and oxidation and reduction potentials all give information, but since electrochemical measurements are especially sensitive to π bonding between metal and ligand they must be interpreted with great caution and are probably the least valuable. However, by combination of these three methods and a modicum of chemical intuition we have reached the following general conclusions concerning charge distribution in certain types of complex.

A simple tertiary phosphine PRR'_2 ($R = R' =$ alkyl or phenyl group) is a good electron donor to a heavy transition-metal ion. In complexes $[MCl_n(PR_3)_n]$ it develops a positive charge approximately equal to or rather greater in size than the negative charge remaining on a complexed chloride ion or developed by a chlorine atom when it is attached to the metal. This charge is *ca.* 0.3 e. The metal is thus essentially neutral, independent of the formal oxidation state of the metal. This explains why such complexes as $[IrCl_3(PR_3)_3]$, $[PtCl_2(PR_3)_2]$, and $[AuCl(PR_3)]$ are so similar in many chemical properties except where oxidation or reduction are involved. When chloride ligands are present in greater numbers than phosphine the metal will tend to develop a positive charge and *vice versa*, although the charges on the ligands especially if they are polarisable adjust to some extent to prevent excessive charge developing on the metal.

Good π-bonding ligands such as carbonyl, trifluorophosphine, and nitrosyl, even when the last is so-called NO^+, are approximately neutral to negative in their complexes, and nitrosyl may even be as electron withdrawing as a chlorine atom. Replacement of a tertiary phosphine by one of those ligands is equivalent to oxidation of the metal by approximately one oxidation unit. Abstraction of a phosphine from the co-ordination sphere with no replacing ligand is also equal to oxidation by approximately two thirds of a unit. Abstraction of a chlorine atom produces a formal reduction of the metal by one unit, but the reduction in o.m.p. is no more than one third of a unit. It requires both the addition of a tertiary phosphine ligand and the abstraction of a chlorine atom to produce a change in the charge on the metal corresponding to a reduction by one oxidation unit. Thus the charge on the metal atom is as dependent on the nature of the formally uncharged ligands as on that of the formally anionic ligands. Oxidation number and real charge are not related although, other things being equal, higher oxidation numbers correspond to greater positive charge on the metal.

Dinitrogen, carbonyl, and nitrosyl are similarly charged in analogous complexes. All usually carry a small negative charge and nitrosyl, even so-called NO^+, is more negatively charged than the other two. In $[ReCl(N_2)(PMe_2Ph)_4]$ and $[ReCl(N_2)(PMe_2Ph)_4]^+$ the dinitrogen ligand carries a small absolute negative charge and is strongly polarised, but the total charge and polarisation is less in the cation than in the neutral species.

The hydride ligand is strongly electron releasing and probably carries a charge of less than a third that carried by a chloride ligand. Thus replacement of chloride in a complex by hydride, although it makes no change in formal oxidation state of the metal, is a real reduction of the metal in the sense that the electron density on the metal is increased by the replacement. Other electropositive anionic ligands, *e.g.*, CH_3^- and $C_6H_5^-$, must be similar and this explains why oxidative addition of methyl iodide occurs to [PtMe(I)(PEt$_3$)$_2$] but not to [PtI$_2$(PEt$_3$)$_2$].[30]

Nitrido- (N^{3-}) and imido- (NR^{2-}) ligands appear to carry no great charge, although their formal charges are high. The *X*-p.e. spectroscopic and electrochemical measurements are uncertain in their significance but we are of the opinion, mainly on the basis of the dipole-moment studies, that they carry rather less charge than chlorine in the complexes which we have investigated, indeed the NPh ligand is probably positively charged.[31]

It must be emphasised that the conclusions we have reached are strictly applicable only to the complexes we have studied, but we are of the opinion that they will be applicable to a much greater area of heavy transition-metal chemistry, especially those conclusions which refer to small or non-conjugated ligands. The charge carried by dinitrogen, carbonyl, and nitrosyl is probably more dependent on the situation in which these ligands find themselves than are the charges carried by tertiary phosphines, halide, and hydride ligands.

EXPERIMENTAL

X-p.e. spectroscopic data were obtained by courtesy of Professor R. Mason and were measured by Dr. J. A. Connor using an A.E.I. ES-200 spectrometer at the University of Manchester. Binding energies are the mean of at least three runs on single samples, and the majority of values were obtained from two samples. Internal carbon(1*s*) (285 eV) was taken as standard.[32] The details of the electrochemical experiments are given in another paper.[23]

Complexes were prepared according to literature methods as detailed below: [ReCl$_2$(PMe$_2$Ph)$_4$];[33] [ReCl$_3$(PMe$_2$Ph)$_3$] and [ReCl$_4$(PMe$_2$Ph)$_2$];[34] [ReCl$_2$(N)(PEtPh$_2$)$_2$] and [ReCl$_2$(N)(PMe$_2$Ph)$_3$];[35] *cis*- and *trans*-[ReCl$_3$(NMe)(PMe$_2$Ph)$_2$], [ReCl$_3$(NPh)(PEtPh$_2$)$_2$];[36] [ReX(N$_2$)(PMe$_2$Ph)$_4$] (X = Cl or Br), [ReCl(N$_2$)(CO)$_2$(PPh$_3$)$_2$], [ReCl(N$_2$)(PMe$_2$Ph)$_4$][FeCl$_4$], [ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$], [ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][FeCl$_4$], [(PhMe$_2$P)$_4$ClRe(N$_2$)MoCl$_4$(OMe)];[20] [ReX(N$_2$)(py)(PMe$_2$Ph)$_3$] (X = Cl or Br), [ReCl(N$_2$)(py)(PMePh$_2$)$_3$];[37] [ReCl(N$_2$)(CO)(PMe$_2$Ph)$_3$], [Re(N$_2$)(PMe$_2$Ph)$_3$(S$_2$CNEt$_2$)];[38] [ReCl(CO)(PMe$_2$Ph)$_4$], [ReCl(CO)(PMe$_2$Ph)$_4$][FeCl$_4$], [ReCl(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$], [ReCl(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]I$_3$;[39] [ReCl$_2$(NO)(PMePh$_2$)$_2$], [ReCl$_2$(NO)(PMePh$_2$)$_3$], [ReCl$_2$(NO)(CO)(PMePh$_2$)$_2$], [ReCl$_3$(NO)(PMePh$_2$)$_2$], Cs[ReCl$_3$(NO)(PMePh$_2$)$_2$], [ReCl$_4$(NO)(PMePh$_2$)$_2$];[37] and [ReH$_5$(PMe$_2$Ph)$_3$].[40]

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