spectrum (Figure 1) is characteristic of oxyanionic complexes,[3,11,12] with the Soret band blue shifted relative to that of the chloro complex and lacking the splitting present in the spectrum of the chloro complex and with a β-band at 557 nm having a weak shoulder at 590 nm. The IR spectrum (Figure 2) shows a strong band at 850 cm^{-1} in the region expected for the Fe–O–Fe stretch.[10,12,13] The ^{1}H NMR spectrum consists of a single resonance at 13.9 ppm, peak width 0.32 ppm at half the peak height. The narrowed peak width compared to pyrrole signals of high-spin complexes is indicative of decreased paramagnetism[14] resulting from antiferromagnetic coupling of the ferric centers, which is evident in the solid-state magnetic moment, $\mu_{\text{eff}} = 1.6\ \mu_B$, at ambient temperature.

The similarity between the features of UV–vis spectra of μ-oxo and oxyanionic complexes generally observed for (porphinato)iron complexes[3,11] is also apparent in the case of the hydroxo pentafluorophenyl complex. The major distinction between the spectra of the μ-oxo dimer and the hydroxo complex is a red shift of both the Soret and β-bands of the hydroxo complex (Figure 1). ^{1}H NMR indicates that water molecules are associated with (hydroxo)((pentafluorophenyl)porphinato)iron(III); hence, the assignment of the hydroxo –OH stretch in the IR spectrum is ambiguous. The IR spectrum shows a prominent absorbance at 3400 cm^{-1}, with a shoulder at 3600 cm^{-1} in the region of –OH stretch. The absence of absorbance between 800 and 900 cm^{-1}, where the Fe–O–Fe stretch is expected[10] and is indeed present in the spectrum of the μ-oxo dimer, confirms the monomeric structure (Figure 2). In contrast to the case of the μ-oxo dimer, the ^{1}H NMR of the hydroxo complex shows a single broad pyrrole resonance at 82 ppm with a width of 3.5 ppm at peak half-height. A broad resonance at ~1.5 ppm is ascribed to the water solvate.[3] The chemical shift of the pyrrole proton is typical of high-spin *meso*-(tetraarylporphinato)iron(III) complexes,[15] and the $S = {}^5/_2$ spin state of iron is further supported by the $\mu_{\text{eff}} = 5.7\ \mu_B$ measured by the Evans method.[16] The EPR spectrum in frozen solution is also typical of axially symmetric high-spin (porphinato)iron(III),[17] showing a strong transition at $g_\perp = 5.9$ and a weaker signal at $g_\parallel = 2$. However, the intensity of the feature at $g = 2$ is higher relative to the $g_\perp$ transition than the $g = 2$ signal in the EPR spectrum of the chloro complex, in accord with observations reported for several other hydroxo compounds.[3]

(Tetrakis(pentafluorophenyl)porphinato)iron(III) is one of several sterically encumbered complexes that have been shown to form mixtures of monomeric hydroxo and dimeric μ-oxo derivatives. We have established conditions for the pentafluorophenyl complex under which each of the two forms will predominate, have developed a procedure for their separation by column chromatography, and have shown that they are sufficiently stable for characterization.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained on a Bruker AC200 at 200 MHz. IR spectra were recorded in a KBr matrix on a Beckman 4250 spectrometer, and UV–vis spectra on a Coleman 124 double-beam spectrophotometer. EPR spectra were recorded in the X-band on a Varian E109 spectrometer in frozen methylene chloride solution at 77 K.

μ-Oxo Dimer. The pure μ-oxo dimer was obtained from the chloro complex or a mixture of μ-oxo dimer and chloro complex (from the metalation of the free base[18]) by dissolving 100 mg of the starting (porphinato)iron in 25 mL of methylene chloride and stirring 4 h with an equal volume of 2 N NaOH. The organic layer was separated, washed twice with water, dried over Na_2SO_4, and chromatographed over neutral alumina (Fisher, A540) with 1:1 benzene/hexane as eluant. The red band containing the μ-oxo dimer was collected and the solid (68 mg) obtained as dark red needles on slow evaporation of solvent. The magnetic moment determined in the solid state at ambient temperature is 1.6 μ_B. UV–vis (toluene) $\lambda_{\max}$ ($\epsilon \times 10^{-3}$): 393 (62.4), 557 (7.0), 590 sh nm. Anal. Calcd for $C_{88}H_{16}N_8F_{40}Fe_2O$: C, 50.97; H, 0.77; N, 5.41; Fe, 5.41. Found: C, 51.58; H, 1.47; N, 5.36; Fe, 5.00.

Hydroxo Complex. Fifty milligrams of μ-oxo dimer was dissolved in 15 mL of methylene chloride, and the solution, along with 0.2 mL of water and 75 mg of *p*-toluenesulfonic acid, was added to a separatory funnel and shaken with periodic monitoring by UV–vis spectroscopy until the spectrum of the sulfonato complex appeared: $\lambda_{\max}$ 350, 406, 510, 630 nm. The solution was dried over sodium sulfate and the solvent removed on a rotary evaporator. The residue was redissolved in 15 mL of methylene chloride and shaken in a separatory funnel with a stoichiometric amount of 1 N NaOH (0.1 mL) until the β-band of the hydroxo complex (563 nm) no longer changed. After the solution was dried over sodium sulfate, the solvent was removed under a stream of nitrogen and the residue chromatographed over alumina with methylene chloride containing 5% acetone or methanol as eluant. The hydroxo complex eluted slowly as a brownish band and was obtained as a solid on removal of solvent under a stream of nitrogen at ambient temperature. UV–vis (methylene chloride) $\lambda_{\max}$ ($\epsilon \times 10^{-3}$): 406 (76), 563 (11.9) nm. A satisfactory analysis of the hydroxo complex could not be obtained, presumably as a result of the inability to remove solvents completely by warming and/or vacuum without generating μ-oxo dimer.

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Registry No. ((Pentafluorophenyl)porphinato)iron(III) μ-oxo dimer, 81245-20-7; chloro((pentafluorophenyl)porphinato)iron(III), 36965-71-6; hydroxo((pentafluorophenyl)porphinato)iron(III), 81278-77-5; ((*p*-tolylsulfonyl)oxy)((pentafluorophenyl)porphinato)iron(III), 103500-01-2.

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Electronegativity and Bonding of Transitional Elements

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Although numerous arbitrary evaluations of electronegativity of transitional elements have been published in most textbooks of inorganic chemistry, reliable evaluation has been prevented, until now, by lack of information concerning homonuclear bond energies and nonpolar covalent radii, especially for gaseous molecules, and by uncertainties concerning the effects of underlying incompletely filled d orbitals and electrons. This paper presents the results of an attempt to determine suitable electronegativity values for the transitional elements and to assess how these values relate to their polar covalent bonding.

Evaluation of Electronegativity

The quantitative theory of polar covalence[1-3] divides the total energy of a polar covalent bond into two contributions, a nonpolar covalent energy and an ionic energy. The total energy if the bond were nonpolar covalent, E_c, is simply the geometric mean of the two homonuclear single covalent bond energies, E_{AA} and E_{BB}, corrected for any difference between the actual bond length, R_o and the sum of the nonpolar covalent radii, R_c, by the factor R_c/R_o:

$$E_c = R_c(E_{AA}E_{BB})^{1/2}/R_o \qquad (1)$$

If the bond were ionic, the energy, E_i, would be the Coulombic energy between unlike unit charges at the observed internuclear distance:

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$$E_i = 33200/R_o \qquad (2)$$

The factor 33 200 converts to kilocalories per mole if R_o is measured in picometers and must be multiplied by 4.184 to convert to kilojoules per mole. The apportionment of the two contributing energies is determined by the partial charges, from which the blending coefficients, t_i and t_c, are calculated. The ionic blending coefficient, t_i, is half the difference between the two partial charges, and the covalent blending coefficient, t_c, is $1.000 - t_i$. The actual energy of the polar covalent bond is then the sum of the two contributions:

$$E = t_cE_c + t_iE_i \qquad (3)$$

This energy is multiplied by 1.488 if the bond is double and 1.787 if the bond is triple.

The partial charges are obtained by application of the principle of electronegativity equalization[4] and the postulate that the electronegativity in a compound is the geometric mean of all the individual atomic electronegativities. The change in electronegativity, ΔS_i, that would correspond to the acquisition of unit charge is given by

$$\Delta S_i = 1.57S^{1/2} \qquad (4)$$

Survey of these four equations shows that in order to determine the energy of a polar covalent bond, the nonpolar covalent radii, the bond length, the electronegativities of the individual atoms, and the homonuclear bond energies must be known. It follows that if the experimental bond energy is known, any one of these other quantities may be back-calculated. To avoid the problems associated with bonding in nonmolecular solids, gaseous molecules are studied. Data were obtained from all available sources.[5-12] Unfortunately, the literature supply of necessary data for gaseous molecules of compounds of transitional elements is both sparse and dubious. Where discrepant bond lengths or heats of formation are reported, they were averaged if quite similar or selected by comparison with data for similar compounds if quite different. Luckily, in the dihalides and trihalides for which bond lengths are available, it was observed that they appear close to linear with atomic number of the transitional element, and the ratios of bond lengths of different halides of the same element appeared constant. On this basis it was possible to determine unknown bond lengths of the dihalides and trihalides of the series from scandium through copper, and to make minor changes believed to be corrections. In other compounds it was sometimes possible to estimate approximate bond lengths from experimental values of similar or related compounds.

The bonds are quite polar in most of the compounds for which data are available. This means that the major contributor to their energy is the ionic contribution, which depends only on the bond length, in addition to the partial charges obtained from the electronegativities. Calculation of the minor contributor, the covalent contribution, on the other hand, requires also a knowledge of homonuclear covalent bond energy and nonpolar covalent radius. These are properties of the hypothetical nonpolar condition and should be constant. They were obtained by interpolation between the calcium- and zinc-group elements. The electronegativity of the transitional elements is left as the sole unknown.

Calculation of this electronegativity can perhaps best be explained by an example. The experimental bond length in $TiF_4(g)$ is 180 pm, and the experimental bond energy is 139.8 kcal/mol of bonds. By interpolation the homonuclear bond energy of Ti is 31.8 kcal. The sum of the nonpolar covalent radii is 233.1 pm. Since studies of the "lone pair bond weakening effect (LPBWE)"[1,2] have shown this effect to be absent in most highly polar metal to halogen bonds, this was assumed to be true also for halides of the transitional elements. The unweakened homonuclear bond energy of fluorine is 113.1 kcal/mol, giving a geometric mean with 31.8 of 60.0. The maximum ionic and covalent energies may now be calculated (from eq 3):

$$E_i(\text{max}) = 33200/180 = 184.4 \text{ kcal}$$
$$E_c(\text{max}) = 60.0 \times 233.1/180 = 77.7 \text{ kcal}$$

Let t_i, the ionic blending coefficient, be x, and t_c be $1 - x$. The experimental bond energy is then

$$139.8 = 184.4x + 77.7 - 77.7x; \quad x = 0.582$$

Since there are five atoms in TiX_4, half the difference between partial charges will be 2.5 times the partial charge of halogen, with appropriate sign. Here 0.582/2.5 = 0.233, so the partial charge of fluorine is –0.233. The partial charge is defined as the ratio of the actual change in electronegativity in forming the compound to the change that would correspond to acquisition of unit charge. The change in electronegativity that would accompany the acquisition of an entire electron is 1.57 times the square root of 4 (eq 4), or 3.14. The partial charge of F is the difference between the molecular electronegativity and 4, divided by 3.14:

$$\delta_F = -0.233 = (S_m - 4.000)/3.14; \quad S_m = 3.269$$

But S_m is also the fifth root of the product of the atomic electronegativities:

$$S_m = 3.269 = (S^4(\text{F}) \times S(\text{Ti}))^{1/5}$$

The electronegativity of titanium, S(Ti), thus obtained is 1.459.

Similar calculations for $TiCl_4$, $TiBr_4$, and TiI_4 produced the following values of the electronegativity of Ti(IV): 1.459, 1.546, and 1.552, the average being 1.504 for the four determinations. This average was then used to calculate the bond energy in each of these molecules, with calculated–experimental values as follows (kcal/mol of bonds): TiF_4, 138.1–139.8; $TiCl_4$, 100.7–102.8% $TiBr_4$, 89.0–87.8; TiI_4, 71.6–70.3. Considering that the extreme range in experimental bond energy varies by a factor of 2, it seems reasonable to accept the calculated electronegativity of titanium as being at least approximately correct for the IV oxidation state.

Values for other transitional elements were similarly calculated. It was recognized that more stable arrangements of d electrons are represented by d^5 and d^{10}. Where bond formation requires disruption of such stable arrangements, the experimental bond energy is expected to be lower by the amount required for such disruption. A measure of the energy so involved is found in ionization energies. The sum of the first two ionization energies is approximately a linear function of the atomic number of transitional element, except for chromium, molybdenum, and copper, where it is respectively 24.6, 31, and 32 kcal too high. These energies were therefore used to correct experimental atomization energies in calculating the electronegativies of these elements. Any bond energies calculated for their compounds must consequently be reduced by the appropriate amount.

Table I summarizes the electronegativity values determined in this way for all of the transitional elements for which appropriate basic data could be found. It also lists the homonuclear bond energies and nonpolar covalent radii. The most interesting discovery is that the values for different oxidation states of the same

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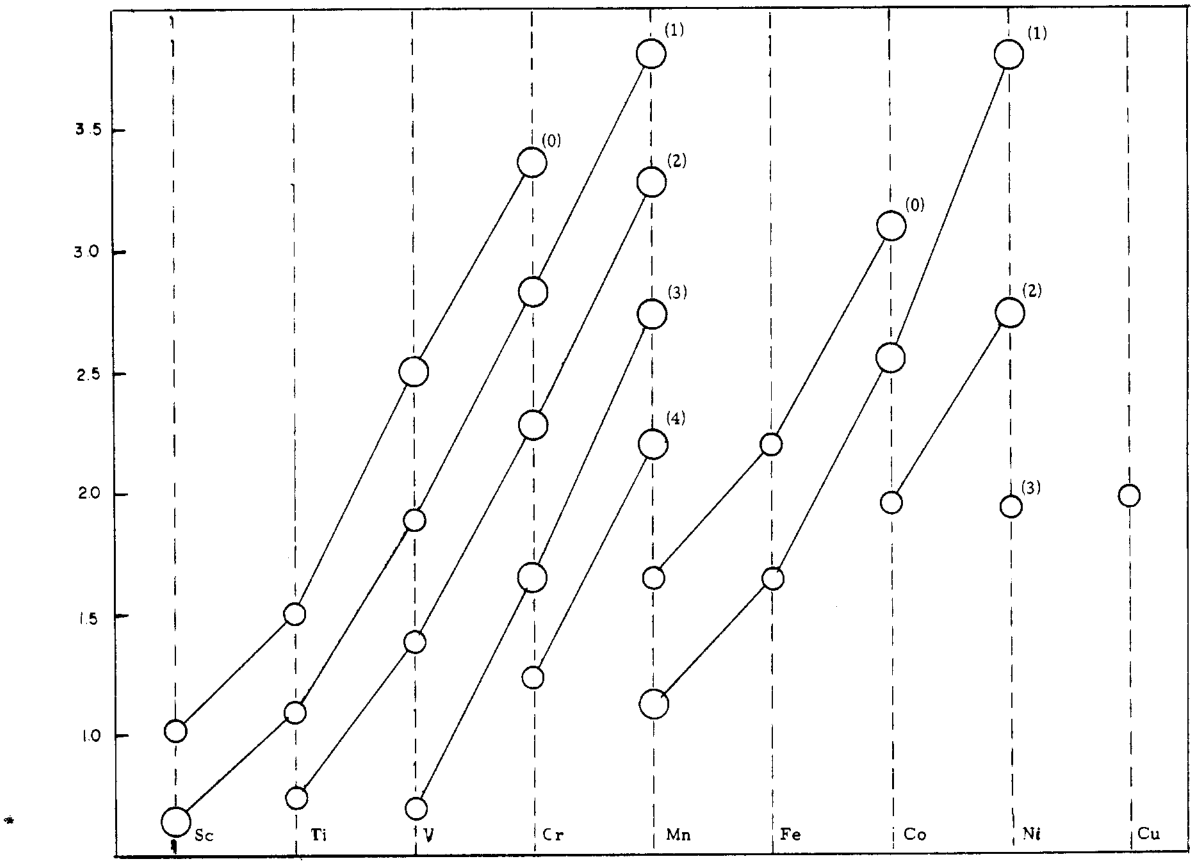

Figure 1. Electronegativities of transitional elements in different oxidation states. (The number of d electrons beyond 0 or 5, that are not involved in bonding, is given.)

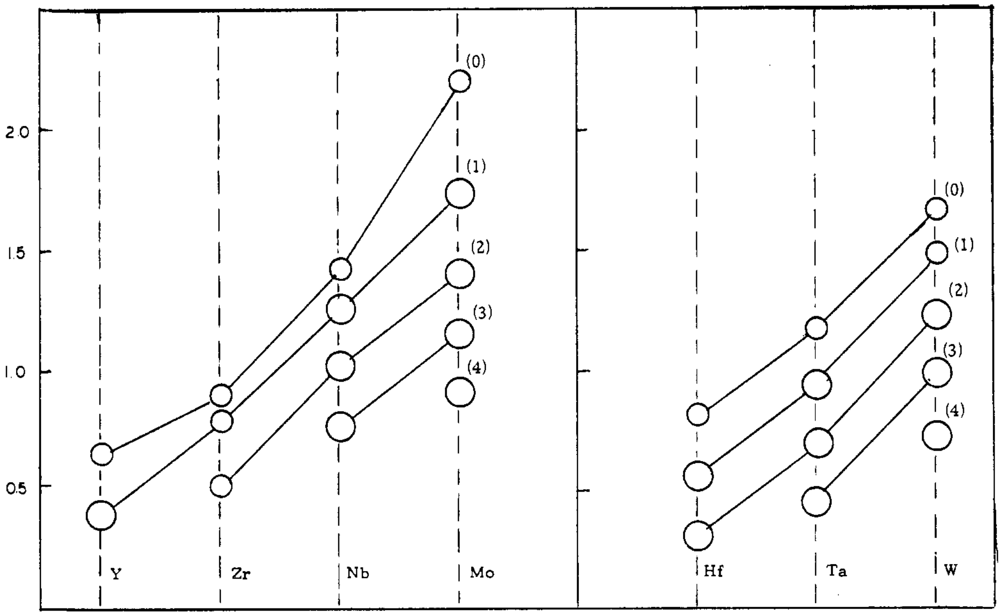

Figure 2. Electronegativities of heavier transitional elements in different oxidation states. (The number of d electrons beyond 0 or 5, that are not involved in the bonding, is given.)

element are significantly different, the electronegativity being reduced for each d electron not involved in the bonding, which appear to be those beyond 0 or 5. By averaging the differences between different oxidation states, it was found that each unbonded electron reduces the electronegativity by about 0.54 for the first series of transitional elements and by about 0.25 for the heavier elements. Use of these average increments allowed rough estimation of values for oxidation states for which basic data are lacking. Figures 1 and 2 permit easy visualization of the way in which electronegativities of the transitional elements change with oxidation state. In these figures, the less well-supported values are indicated by larger circles.

Testing the Validity of the New Electronegativities

Practically all electronegativity scales have values suggesting the presence and approximate extent of bond polarity and its consequences, but only the scale based on relative compactness of electronic spheres has been subjected to quantitative testing. The successful accurate calculation of thousands of bond energies in hundreds of compounds involving practically all major-group

Table I. Covalent Radius, Homonuclear Bond Energy, and Electronegativity of Transitional Elements

element	r_c, pm	E_H, kcal	S(II)	S(III)	S(IV)	S(V)	S(VI)
Sc	169.5	31.3	0.64 (1)[a]	1.02 (3)			
Y	186.8	25.1	(0.40)[b]	0.65 (4)			
Ti	165.0	31.8	0.73 (4)	1.09 (4)	1.50 (4)		
Zr	182.6	25.7	0.52 (4)	0.79 (4)	0.90 (4)		
Hf	180	15.6	(0.31)	(0.56)	0.81 (4)		
V	160.5	32.3	0.69 (3)	1.39 (2)	1.89 (2)	2.51 (1)	
Nb	178.4	26.3	(0.77)	1.02 (1)	1.25 (1)	1.42 (3)	
Ta	176	14.7	(0.44)	(0.69)	0.94 (1)	1.17 (2)	
Cr[c]	156.0	32.8	1.24 (3)	1.66 (1)	2.29 (1)	(2.83)	(3.37)
Mo[c]	174.2	26.9	(0.90)	(1.15)	1.40 (1)	1.73 (1)	2.20 (2)
W	173	13.8	(0.73)	(0.98)	(1.23)	1.48 (2)	1.67 (3)
Mn	151.6	33.3	1.66 (4)	(2.20)	(2.74)	(3.28)	(3.82)
Fe	147.1	33.8	1.64 (3)	2.20 (4)			
Co	142.6	34.3	1.96 (4)	2.56 (1)	(3.10)		
Ni	138.1	34.8	1.94 (3)	2.73 (1)	(3.27)	(3.81)	
Cu[c]	133.6	35.3	1.98 (2)				

[a] Number in parentheses is of compounds averaged. [b] Rough estimates based on an average difference between oxidation states of 0.54 for first transitional series and 0.25 for later series. [c] Values determined from bond energies corrected for loss by disruption of d^5 or d^{10}.

Table II. Application of New Electronegativities to Bond Energy Calculation in Compounds of First-Series Transitional Elements

compd	$-\delta_X$	R_c, pm	R_o, pm	E_c, kcal	E_i, kcal	E(calcd), kcal	E(exptl), kcal
ScF_3	0.354	237.6	192.6	19.3	127.1	146.4	148.3
$ScCl_3$	0.299	268.9	232	20.4	89.3	109.7	108.1
$ScBr_3$	0.271	283.7	244.0	21.3	72.6	95.9	92.1
ScI_3	0.222	302.8	271.5	21.9	57.5	79.4	76.9
TiF_2	0.551	233.1	172.9	12.7	142.8	155.5	157.3
$TiCl_2$	0.481	264.4	230	15.3	104.0	119.3	122.4
$TiBr_2$	0.445	279.2	246	16.2	90.2	106.4	104.3
TiI_2	0.381	298.3	266	18.0	71.3	89.3	84.0
TiF_3	0.352	233.1	190	21.6	123.5	145.1	151.2
$TiCl_3$	0.297	264.4	230	22.1	86.2	108.3	109.7
$TiBr_3$	0.269	279.2	240	22.9	75.0	97.9	94.1
TiI_3	0.220	298.3	271.5	22.8	54.1	76.9	75.0
TiF_4	0.226	233.1	180	33.7	104.4	138.1	139.8
$TiCl_4$	0.183	264.4	219	31.3	69.4	100.7	102.8
$TiBr_4$	0.161	279.2	231	31.1	57.9	89.0	87.8
TiI_4	0.123	298.3	250	31.0	40.6	71.6	70.3
TiO_2	0.312	235.2	162	44.4	95.9	140.3	147 ± 5
$TiOF_2$							
Ti—O‴	0.197	235.2	162	42.1	101.6	151.2	
Ti═O″	0.197	235.2	162	52.5	146.1		
Ti—F′	0.299	233.1	174	21.8	104.4 (×2)	$\underline{252.4}$	
						425.0	431.4
$TiOCl_2$							
Ti—O‴	0.267	235.2	162	43.5	98.2	170.1	
Ti═O″	0.267	235.2	162	52.5	146.1		
Ti—Cl′	0.212	264.4	220	28.3	68.2 (×2)	$\underline{199.4}$	
						369.5	361
VCl_2	0.495	259.9	227	14.2	108.7	122.9	121.1
VBr_2	0.459	274.7	243	15.3	94.1	109.4	107.0
VI_2	0.395	293.8	262	17.3	75.0	92.3	96.5
VCl_3	0.236	259.9	226	28.5	71.4	99.9	102.7
VBr_3	0.209	274.7	236.5	28.6	60.8	89.4	86.6
VCl_4	0.136	259.9	214	38.6	52.7	91.3	91.1
VBr_4	0.116	274.7	230	37.3	40.3	77.6	77.6
CrF_2	0.412	224.1	186	28.0	110.2	138.2	127.0
$CrCl_2$	0.373	255.4	223.5	26.7	76.9	103.6	104.2
$CrBr_2$	0.311	270.2	239	26.3	64.9	91.2	95.0
CrI_2	0.250	289.3	258	26.6	48.3	74.9	71.0
MnF_2	0.325	219.7	184	37.6	87.9	125.5	110.3
$MnCl_2$	0.260	251.0	220.5	34.0	58.8	92.8	94.4
$MnBr_2$	0.227	265.8	236	32.8	48.0	80.8	79.6
MnI_2	0.168	284.9	255	31.9	32.8	64.7	64.4
FeF_2	0.328	215.2	181	32.3	90.2	127.5	115.2
$FeCl_2$	0.263	246.5	217	33.9	60.4	94.3	96.3
$FeBr_2$	0.230	261.3	232.5	32.7	49.3	82.0	82.0
FeI_2	0.171	280.4	251	31.9	34.0	65.9	64.2
FeF_3	0.178	215.2	177	48.5	66.4	114.9	117.5
$FeCl_3$	0.129	246.5	214.5	42.2	39.7	81.9	82.4
$FeBr_3$	0.105	261.3	224.5	41.0	30.7	71.7	69.7
FeI_3	0.061	280.4	250	16.0	54.0	54.0	53.0
CoF_2	0.302	210.7	178.5	40.2	84.3	124.5	111.7
$CoCl_2$	0.205	242.0	214	38.8	47.8	86.6	91.4
$CoBr_2$	0.173	256.8	229	37.1	37.7	74.8	77.9
CoI_2	0.116	275.9	247.5	35.8	23.3	59.1	62.7
NiF_2	0.274	206.2	176	43.3	77.4	120.7	109.6
$NiCl_2$	0.210	237.5	211	38.6	49.6	88.2	87.0
$NiBr_2$	0.178	252.3	226	36.8	39.3	76.1	76.0
NiI_2	0.121	271.4	244	35.6	24.6	60.2	61.3
CuF_2	0.265	201.7	173	44.4	76.3	120.7	109.6
$CuCl_2$	0.202	233.0	208	39.2	48.4	87.6	86.7
$CuBr_2$	0.171	247.8	222	37.7	38.4	76.1	77.1

elements[1-3] has provided powerful support of the validity of the electronegativities used in the calculations. Even though the new values presented here for the transitional elements have been derived from experimental bond energies, it is appropriate to subject them to the same test. Table II and III provide 90 examples, indeed all that could be found, including a number not used in the original calculations. The average difference between calculated and experimental bond energy is less than 3%, despite averaging in several examples of differences exceeding 10%. Although this is less satisfactory than the usual 1-2% accuracy of calculations involving the major-group elements, it seems reasonably supportive of the approximate validity of the new electronegativities. Indeed, a difference between calculated and experimental values does not necessarily imply inaccuracy in the simple theory of polar covalence but may merely emphasize the need for more accurate experimental determinations of bond length and heat of formation. There seems no doubt that the values reported herein can be refined and improved further when better basic data become available, but even in their present state, they can be very helpful toward achieving a better understanding of chemistry.

Further Applications

It has long been recognized that "first-row" transitional elements differ from the heavier elements of their respective periodic groups in consistent and significant ways. They are commonly found in their lower oxidation states but tend to be unstable and highly oxidizing in their higher oxidation states. In contrast, the heavier elements of these groups are much better known in their higher oxidation states, which are quite stable. One would not expect such a difference, for instance, from the electronegativities of Cr, 1.24, and W, 0.7, in the II state, both relatively low. However, in the VI state, chromium only forms CrF_6 at high fluorine pressures and very low temperatures, and it is stable only below −100 °C,[10] whereas WF_6 is quite stable. Figure 3 is provided to help visualization of the differences. Note that chromium in the VI state appears to resemble bromine in electronegativity, whereas tungsten(VI) has a value of about 1.7. This means that the bonds are much more polar in WF_6 and hence much stronger.

The ultimate explanation must of course lie in the differences in atomic structure. If only the core electrons of each element are considered to occupy the sphere defined by the nonpolar covalent radius, there are nearly 3 times more electrons per unit volume in the tungsten atom than in the chromium atom. Evidently the effective nuclear charge that can be sensed at the core surface is smaller in the more compact atom. Even though the effect of each nonbonding d electron is smaller in the former, the initial electronegativity at maximum valence is so much lower that, even in the II oxidation state, tungsten is still less electronegative than chromium, although they are not nearly so different here as in the higher oxidation states. As shown in Figure 3, in their higher oxidation states, chromium, manganese, cobalt, nickel, and

Table III. Calculation of Bond Energy in Compounds of Heavier Transitional Elements

compd	$-\delta_X$	R_c, pm	R_o, pm	E_c, kcal	E_i, kcal	E(calcd), kcal	E(exptl), kcal
YF_3	0.466	254.9	204	4.6	151.5	156.1	155.3
YCl_3	0.407	286.2	247	9.2	109.4	118.6	122.5
YBr_3	0.378	301.0	263	10.7	75.3	106.0	101.9
YI_3	0.324	320.1	280	13.4	76.9	90.3	91.7
ZrF_2	0.627	250.7	192	4.2	162.7	166.9	159.2
$ZrCl_2$	0.556	282	230	8.7	120.3	129.0	122.9
$ZrBr_2$	0.519	296.8	247	10.3	104.7	115.0	120.3
ZrI_2	0.453	315.9	266	12.8	84.9	97.7	106.2
ZrF_3	0.424	250.7	193	10.6	145.8	156.4	155.6
$ZrCl_3$	0.367	282	230	14.1	105.8	119.9	118.6
$ZrBr_3$	0.338	296.8	239	15.6	93.8	109.4	109.5
ZrI_3	0.289	315.9	259	17.6	73.2	90.8	91.7
ZrF_4	0.328	250.7	190.2	12.9	143.1	156.0	156.3
$ZrCl_4$	0.280	282	232	15.6	100.3	115.9	117.3
$ZrBr_4$	0.258	298.8	247	16.5	86.8	103.3	102.8
ZrI_4	0.214	315.9	268	18.5	66.2	84.7	83.2
NbF_5	0.202	246.5	188	28.1	107.2	135.3	136.5
$NbCl_5$	0.165	277.8	226.5	27.0	72.6	99.6	97.8
$NbBr_5$	0.146	292.6	245.5	26.2	59.2	85.4	82.4
MoF_6	0.105	242.3	182.5	46.4	66.5	112.9	112.8
$MoCl_6$	0.076	273.6	226	39.0	38.9	77.9	77.9
HfF_4	0.348	248.1	190.9	7.2	151.1	158.3	155.7
$HfCl_4$	0.299	279.4	233	10.1	106.6	116.7	119.0
$TaCl_5$	0.099	275.4	230	15.8	85.5	101.3	102.8
$TaBr_5$	0.089	290.2	244.5	16.2	72.5	88.7	87.4
TaI_5	0.072	309.3	266	16.8	53.5	70.3	82.3
WF_6	0.150	241.1	182.9	24.7	95.3	120.0	121.7
WCl_6	0.119	272.4	226	22.2	60.9	83.1	83.2
WBr_6	0.103	287.2	240	21.8	49.7	71.5	70.2
WCl_5	0.157	272.4	226	20.1	69.4	89.5	89.5
WBr_5	0.139	287.2	240	19.9	57.5	77.4	77.4
ZrO_2	0.453	252.8	171.1	24.4	131.9	156.3	166.5 ± 6
MoO_3							
$Mo{=}O''$	0.145	244.4	180	61.8	79.6	141.4	140.7
WO_3							
$W{=}O''$	0.217	243.2	181	34.8	118.4	153.2	150.7
WOF_4							
$W{-}F'''$	0.190	241.1	183	25.1	93.8 (×4)	475.7	
$W{\equiv}O'''$	0.083	243.2	181	48.8	151.7	200.5	
						676.2	676.7 ± 6
$WOCl_4$							
$W{-}Cl'''$	0.128	272.4	226	22.3	60.7 (×4)	331.9	
$W{\equiv}O'''$	0.185	243.2	181	50.8	144.6	195.4	
						527.3	515.7 × 5
WO_2Cl_2							
$W{-}Cl'$	0.142	272.4	226	20.1	60.4 (×2)	161.0	
$W{\equiv}O'''$	0.198	243.2	181	50.9	143.9 (×2)	389.5	
						550.5	540.7 ± 6

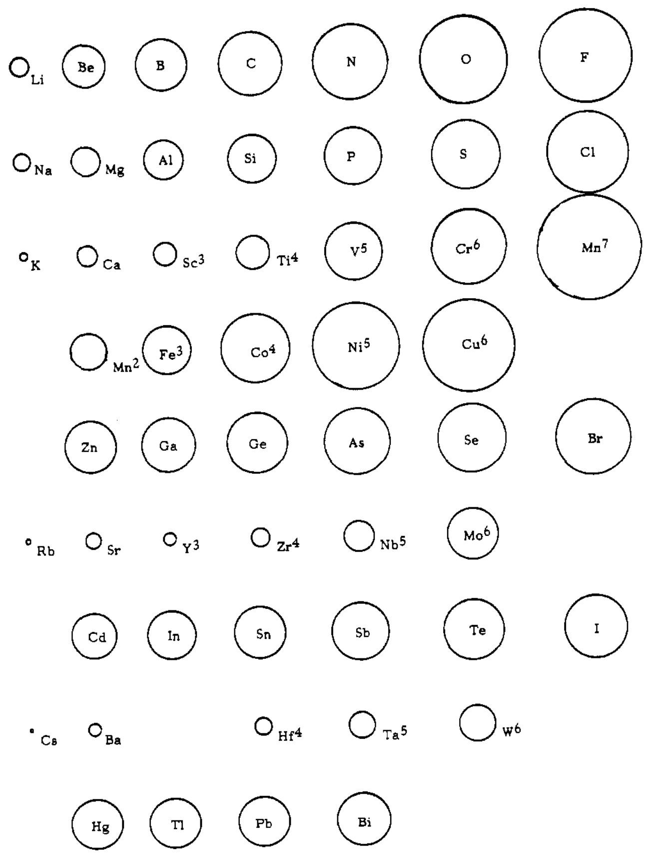

Figure 3. Relative electronegativities. (Superscript number is the oxidation number; this designation is suggested as more convenient than the usual Roman numerals in parentheses.)

copper all resemble the halogens in their electronegativity, but this is not true of the heavier elements of these transitional groups. The high values are of course estimates made from extensive extrapolation and are not to be considered accurate, but they do present a picture that is at least qualitatively correct.

No doubt the new electronegativity values will provide useful insights concerning the chemistry of transitional elements that will correspond to earlier results from application of partial charges and bond energies to major-group chemistry. They should also contribute to better understanding of the solid state that transitional elements exhibit in most of their compounds.

Registry No. Sc, 7440-20-2; Y, 7440-65-5; Ti, 7440-32-6; Zr, 7440-67-7; Hf, 7440-58-6; V, 7440-62-2; Nb, 7440-03-1; Ta, 7440-25-7; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8.

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Pentadienyl-Metal-Phosphine Chemistry. 7.[1] Synthesis, Solid-State Structure, and Solution Dynamics of (η^5-Pentadienyl)tris(phosphine)rhenium Complexes. Measurement of the Rotational Barrier for the Pentadienyl Ligand

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Electron-rich cyclopentadienyl–metal–phosphine complexes have recently attracted a great deal of interest because of their ability to activate bonds that are generally resistant to activation. For example, Bergman[2] has recently shown that $(\eta^5\text{-cp})\text{Re}(\text{PMe}_3)_3$ will, upon photolysis, activate C–H bonds in methane, while Green[3] has demonstrated that $(\eta^5\text{-cp})\text{Mn}(\text{PMe}_3)_3$ will activate C–O bonds in carbon dioxide.

We have initiated a systematic study of the chemistry of electron-rich metal–phosphine complexes containing the acyclic pentadienyl ligand (pd).[1,4] These complexes are expected to be even more electron-rich than their cyclopentadienyl analogues[5]

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(1) For the previous paper in this series, see: Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics*, in press.

(2) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358.

(3) Green, M. L. H.; Joyner, D. S.; Wallis, J.; Bell, J. P. Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

(4) (a) Bleeke, J. R.; Hays, M. K. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (c) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194.

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