isomeric species even at the lowest temperatures accessible.

The ^{13}C chemical shifts of the bound carbon atoms C(7) and C(8) of the acetylene as well as the amidinium center C(9) of the ligand are of some interest, since such shifts frequently provide an indication of the character of these atoms.[12] For 4 and **5a–c** the C_α and C_β resonances of the μ_2-‖-acetylene lie very close together in the range 147.1–171.7 ppm, in sharp contrast to the case for the precursor isonitrile adducts, which exhibit $\Delta(\delta_{C_\alpha}-\delta_{C_\beta})$ values of 172–142 ppm. The shifts in 4 and **5a–c** are somewhat downfield of the range for olefinic carbon signals (110–150 ppm)[18] but upfield of metal-bound carbenes. Clearly the electronic environments of C(7) and C(8) are not dramatically different in these compounds. The ^{13}C resonances for C(9) in 4 and **5a–c** were easily detected as nitrogen quadrupole broadened signals in the range 99–109 ppm.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work in the form of operating grants (A.J.C.), a postgraduate scholarship (A.A.C.), and an International Scientific Exchange Award (to E.S. and A.J.C.).

Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, and phenyl ring bond lengths and angles (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(18) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 289.

Distortions in the "Legs" of Four-Legged Piano-Stool Structures[†]

Rinaldo Poli

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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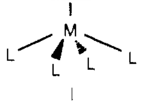
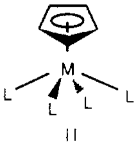
An analysis of existing four-legged piano-stool structures ($M(Ar)L_4$, $M(pd)L_4$; Ar = η^6-arene, pd = η^5-pentadienyl, L = two-electron-donor ligand) is presented. The dependency of the angle θ between the M–L and the M–Ar or M–pd vectors on the electronic structure and on the π-bonding ability of the ligand L is examined. The relevant conclusions from this analysis are that (i) the metal d_{z^2} orbital is a better base than the d_{xy} orbital, (ii) phosphine ligands exhibit distortions typical of π-acceptor ligands, (iii) halide ligands function as π donors in compounds with an electron count lower than 18, and (iv) the θ angle for a particular ligand strongly depends also on the nature of the ligand that is trans to it. The results of this anlysis can be used to qualitatively assess the π-bonding abilities of metals and ligands from structural data.

Introduction

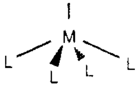
"Four-legged piano stool" is the commonly used terminology for structures of type I–III, i.e. containing a π-bonded cyclopolyene or cyclopolyenyl ligand and four additional σ-bonded two-electron-donor ligands (L). The structures may also be viewed as pseudo square pyramidal (sp) when the π-bonded ligand is considered to occupy a single coordination position.



I



II



III

A theoretical analysis of $MCpL_4$ compounds (Cp = η^5-cyclopentadienyl), type II, has been presented by Hoffmann.[1] In that work, the preference for the piano-stool structure over other possible isomers (isomeric pseudo-sp or pseudo-tbp geometries) was rationalized. The distortion of the Cp ring (tilting toward a η^3,η^2 conformation), which is sometimes observed experimentally, was also explained. However, the experimentally observed distortion of the four L ligands from the ideal pseudo-sp geometry (as measured by the angle L–M–Ct, θ; Ct = centroid of the Cp ligand) was not fully addressed.

We have recently prepared and structurally characterized a few members of the class of stable 17-electron radicals $MoCpX_2L_2$ (X = Cl, Br, I; L = phosphine)[2,3] and noticed distortions in the MoX_2L_2 moiety that differ substantially from those usually observed for 18-electron compounds of similar structure. This observation prompted us to analyze the origin of these distortions in more detail. We report here the results of this analysis, which allows the rationalization of our structural data and also of other data that are already available in the literature.

The Model

The electronic structures corresponding to the molecular structures I–III are expected to be qualitatively the same, since all three π ligands have a lower energy orbital involved in a σ interaction with the metal, followed at higher energy by two degenerate orbitals for a π donation (for the sake of homogeneity, we shall consider the cyclobutadiene ligand as an aromatic $C_4H_4^{2-}$, six-electron-donor system) and at least one orbital for a δ back-bonding interaction with the metal d_{xy} orbital (the arene and Cp ligands have two degenerate orbitals of this type, but only one can be used for δ back-bonding since the metal $d_{x^2-y^2}$ orbital is used up for the σ interaction with the four L ligands). Of the

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(1) Kubácek, P.; Hoffman, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

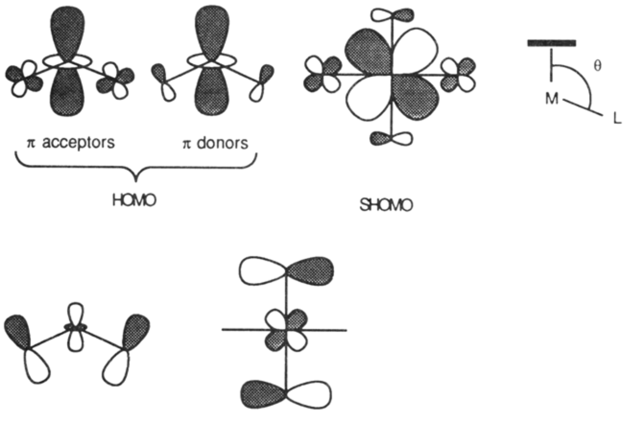
(2) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

(3) Owens, B. E.; Krueger, S. T.; Poli, R. *Inorg. Chem.*, in press.

[†] Dedicated to Prof. F. Albert Cotton on the occasion of his 60th birthday.

0276-7333/90/2309-1892$02.50/0

Chart I



five metal d orbitals, besides the $x^2 - y^2$ orbital just discussed, the xz and yz orbitals are engaged in the strong covalent π interaction with the π-bonded ligand, and only the xy and z^2 orbitals remain available to accommodate the metal electrons. When four metal electrons fill up these two orbitals, a closed-shell 18-electron configuration is obtained. Comprehensive MO analyses for $MCpL_4$ molecules in general (by the extended Hückel method),[1] and for the $MoCpX_2(PH_3)_2$ (X = Cl, I) molecules in particular (by the Fenske–Hall method),[2] are available. In all cases it is found that the HOMO is primarily z^2 in character and the second highest occupied MO (SHOMO) is the xy-based orbital. The same relative ordering has been proposed for the (benzene)ML_4 complexes.[4a]

The results obtained by the Fenske–Hall method are particularly illuminating because model molecules containing at the same time potentially π-acceptor as well as potentially π-donor ligands, that is $MoCpX_2(PH_3)_2$ (X = Cl, I), were used for the calculations.[2] It was found that both the HOMO and the SHOMO have substantial contribution from P 3d orbitals (π bonding) and from X valence p orbitals (π antibonding)[2] as shown in Chart I. No contribution was found from the H 1s orbitals, as could be expected if the π-accepting orbitals on the phosphine ligands had a component from the P–H σ* orbitals. Arguments in favor of metal π donation into linear combinations of P–X σ* orbitals vs phosphorus d orbitals in phosphine-type ligands have been presented.[4b,c] The nature of the phosphorus π-accepting orbitals, however, does not affect the qualitative discussion presented in this account, since both types discussed transform in an identical manner under the molecular symmetry operations. In the $MoCpX_2(PH_3)_2$ compounds,[2] the Mo–X π-antibonding component in the HOMO and SHOMO is counterbalanced by a π-bonding contribution in lower energy MO's (IV and V, mainly halogen lone pairs in character). The X and the PH_3 ligands interact with both the z^2 and xy metal d orbitals because they are double-faced with respect to π interactions. A single-faced π ligand (either acceptor, e.g. olefin, carbene, or donor, e.g. amide) would interact only with one metal orbital (either z^2 or xy), and its orientation in the structure determines which of the two it interacts with.

The drawings illustrated in Chart I can be easily extrapolated to compounds with a different π-donor (X)/π-acceptor (L) ratio (that is, ML_4, MXL_3, MX_3L, and MX_4). In each case double-faced π acceptors will form bonding combinations with both the z^2 and xy metal orbitals, and double-faced π donors will use the same orbitals to form bonding and antibonding combinations, the latter being part of the two highest occupied, metal-based MO's.

Let us now examine the effect of π interactions on the coordination geometry, in particular on the angle θ between the M–L bond and the M–π-ligand (centroid) vector. The argument can be visualized for the $MoCpX_2L_2$ compounds with the aid of Chart I but can be easily extended to four-legged piano-stool molecules with arene or cyclobutadiene and with a different number of π-acceptor and π-donor ligands. For compounds where π effects are absent or negligible, the angles θ are aproximately 110° (vide infra). The following two simple rules can be formulated. (1) The HOMO is stabilized by increasing θ for the π-acceptor ligands, thus allowing a greater π-bonding interaction. As discussed by Hoffmann,[1] the overlap of a probe acceptor orbital on the ligand with the z^2 metal orbital is maximal at $\theta = 135°$. The HOMO is also stabilized by decreasing θ for the π-donor ligands in order to minimize the unfavorable π-antibonding interaction. The minimal overlap is obtained for $\theta = 90°$. (2) The SHOMO is stabilized by exactly opposite distortions. The maximal overlap of a π-acceptor orbital with d_{xy} is at $\theta = 90°$, whereas the minimal overlap of a π-donor orbital is at $\theta = 180°$.

The experimental value of θ is also influenced by other interactions in MO's of lower energy. These are primarily the σ interactions of L with metal hybrids and the π-bonding interactions illustrated in IV and V. The qualitative effect of the latter on the value of θ can be worked out easily in a way similar to that presented in rules 1 and 2 for the HOMO and the SHOMO. However, the relative change in the angle θ for compounds with a different electron count will mainly depend on the π interactions with the two highest energy MO's. Steric effects, when they are believed to be important, will be examined case by case.

On the basis of the previous rules, we can predict the following trends. For π neutral ligands (e.g. H, CH_3, SiR_3, etc.) the θ angle will be determined solely by the σ-bonding pattern and is not expected to depend on the metal electron count (the two highest occupied MO's do not have a M–L σ contribution). π donors are expected to behave as π-neutral ligands in 18-electron compounds for obvious reasons. For compounds with 17, 16 (low spin), and 15 electrons, the metal d_{z^2} orbital has less electrons than the d_{xy} orbital. According to rules 1 and 2, the θ angle is expected to increase with respect to 18-electron compounds. For 14-electron compounds, both the z^2 and the xy orbitals on the metal are empty and the ligand lone pairs can now π-donate into both metal orbitals. The distortion is expected to depend upon which of these two π donations (as represented in IV and V) is more effective but is not expected to be as large as for 15-electron and low-spin (ls) 16-electron compounds. In summation, the following trend for the angle θ is expected for π-donor ligands: 18e < 17e < 16e (ls) > 15e > 14e. In high-spin 16-electron complexes, i.e. when both the z^2 and the xy orbitals are singly occupied, a distortion qualitatively similar to that observed for 14-electron compounds (but quantitatively half as effective) should be found.

For π acids, the θ angle in 18-electron compounds is expected to experience a distortion that will depend upon which among the z^2 and xy metal orbitals is the strongest π donor. If the z^2 orbital is the better base (as seems likely,

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[4] (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033. (c) Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

Table I. θ Angles (deg) for Selected $M(\eta^n\text{-}C_nR_n)L_1L_2L_3L_4$ 18-Electron Piano-Stool Compounds (L_1 Trans to L_3; L_2 Trans to L_4)

M	C_nR_n	L_1	L_2	L_3	L_4	θ_1	θ_2	θ_3	θ_4	ref
Type I										
V$^+$	Dur[a]	CO	CO	CO	CO	121.7	118.9	121.3	120.8	6
Mo$^+$	Mes[b]	I	CO	CO	CO	113.7	123.8	118.2	126.8	7
Mo$^+$	C_6Me_6	I	CO	CO	CO	116.9	122.8	118.9	125.2	7[c]
						115.0	123.6	120.8	124.4	8[d]
						117.9	125.2	116.1	125.2	8[e]
Mo	C_6H_6	Me	$PPhMe_2$	Me	$PPhMe_2$	109.9	130.4	109.2	129.0	9
Mo	Tol[f]	Me	$PPhMe_2$	Me	$PPhMe_2$	108.5	130.7	109.1	129.0	9
W$^+$	Mes[b]	I	CO	CO	CO	111	119	125	131	7
Type II										
Ti$^-$	Cp	CO	CO	CO	CO	120.4	124.8	126.6	122.9	10[g]
V	Cp	CO	CO	CO	CO	117.7	119.8	119.8	117.7	11
V	Cp	tht[h]	CO	CO	CO	118.3	119.6	117.3	122.6	12
V	Cp	bpy		CO	CO	115.8	115.8	117.2	117.2	12
V	Cp	dppe[i]		CO	CO	116.7	118.0	116.9	115.3	13
Nb	Cp	CO	CO	CO	CO	118.5	123.6	123.6	118.5	14
Mo	Cp	Cl	CO	CO	CO	111.8	124.9	111.6	125.3	15, 16
Mo	Cp	C_3F_7	CO	CO	CO	110.1	121.1	118.0	122.0	17
Mo	Az[j]	CH_3	CO	CO	CO	113.1	125.8	115.3	127.8	18
Mo	Cp	HgCl	CO	CO	CO	112.0	123.4	119.2	123.7	16, 19
Mo	Cp	CH_2COOH	CO	CO	CO	112.2	123.0	116.0	128.5	20
Mo	Cp	I	CO	PPh_3	CO	109.1	126.1	109.9	128.4	21
Mo	Cp	I	CO	$P(OMe)_3$	CO	111.1	123.4	113.3	127.6	22
Mo	Cp′[k]	I	CO	$P(OMe)_3$	CO	111.2	123.0	111.2	129.6	22
Mo	Cp	I	CO	CNPh	CO	112.2	126.7	110.1	128.8	23
Mo	Cp	$COCH_3$	CO	PPh_3	CO	110.8	125.2	116.5	126.2	24
Mo	Cp	$GePh_3$	CO	CPh(OEt)	CO	112.2	124.7	115.9	128.6	25
Mo	Cp	I	PBu_3	CO	CO	112.5	121.0	112.4	119.8	26
Mo	Cp	Br	PPh_3	CO	CO	120.6	114.8	118.8	113.8	27a
						119.3	116.8	117.9	118.0	27a[l]
Mo	Cp	Cl	dppe[i]		CO	106.8	124.8	110.2	121.5	21
Mo$^+$	Cp	dmpe		dmpe[m]		111.0	114.6	115.4	112.7	27b
						110.0	114.0	117.1	116.7	27b[l]
W	Cp	Cl	CO	CO	CO	110.9	125.1	111.7	125.7	16
W	Cp	Ph	CO	CO	CO	119.1	121.5	119.7	127.4	28
						116.6	126.4	115.1	129.6	28[l]
W	Cp	$GaMe_2$	CO	CO	CO	117.5	128.0	119.0	127.1	29
W	Cp	$AuPPh_3$	CO	CO	CO	112.9	125.0	123.2	125.4	30
W	Cp	X-L[n]		PMe_3	CO			113.2	119.4	31
Mn$^+$	Cp	$SnCl_3$	CO	PPh_3	CO	111.6	122.2	117.3	121.9	32
Re	Cp*	Br	CO	Br	CO	104.8	126.6	116.2	128.7	33
Re	Cp*	I	I	CO	CO	113.9	117.1	116.9	120.9	33
Re	Cp	H	PPh_3	H	PPh_3	107	125.3	115	126.1	34
Re$^+$	Cp	H	PPh_3	MeCN	PPh_3		123.1	114	125.7	35
Re$^+$	pd*[o]	H	PMe_2Ph	PMe_2Ph	PMe_2Ph	100	125.5	113.7	128.2	36
Rh	Cp*	H	$SiEt_3$	H	$SiEt_3$	131.8	125.9	133.4	125.9	37

[a] Dur = durene (1,2,4,5-$C_6H_2Me_4$). [b] Mes = mesitylene (1,3,5-$C_6H_3Me_3$). [c] Salt of $[MoI_3(CO)_4]^-$. [d] Salt of $[MoI_2(I_3)(CO)_4]^-$. [e] Salt of I_5^-. [f] Tol = toluene. [g] Positional parameters obtained from the Cambridge Crystallographic Database. [h] tht = tetrahydrothiophene. [i] dppe = bis(diphenylphosphino)ethane. [j] $[Mo(Az)(CH_3)(CO)_3]_2$ (Az = $^1/_2$ 4,4′-diazulene). [k] Cp′ = η^5-C_5H_4Me. [l] Second independent molecule in the asymmetric unit. [m] dmpe = bis(dimethylphosphino)ethane. [n] X-L = C(Me)CO. [o] pd* = 2,4-dimethylpentadienyl.

since it has a higher energy), the angle is expected to be greater with respect to that of π-neutral ligands. If, on the other hand, the *xy* orbital is the better base, the angle is expected to be smaller with respect to that of π neutral ligands. When electrons are removed from the z^2 orbital, according to rules 1 and 2, the θ angle is expected to decrease because π donation from *xy* will become more important. On the other hand, removing d electrons will decrease the overall π-donating ability of the metal until, for 14-electron compounds, there are no more metal d electrons available for π back-bonding, and if potential π-acceptor ligands are present, they should behave as π neutral ligands. The following trend is expected for the θ angle of π acceptors: 18e > 17e > 16 e (ls) < 15e < 14e. For high-spin 16-electron compounds a situation similar to that of 18-electron compounds can be described.

Results

Most of the four-legged piano-stool structures available in the literature have an 18-electron configuration. However, a few examples of 17–14-electron compounds have been described recently. We have collected the θ angles for a wide variety of published crystal structures of types I and II. Although compounds of type III are known,[5a] we are not aware that any of these have been structurally characterized.[5b] Eighteen-electron complexes[6-37] are re-

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(5) (a) Connelly, N. G.; Kelly, R. L.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1981**, 34. (b) The X-ray structure of $Mo(\eta^4\text{-}C_4H_4)(CO)_3(PPh_3)$ has been quoted as a private communication in: Amiet, R. G.; Reeves, P. C.; Pettit, R. *Chem. Commun.* **1967**, 1208.

(6) Calderazzo, F.; Pampaloni, G.; Vitali, D.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1982**, 1993.

(7) Barbati, A.; Calderazzo, F.; Poli, R.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1986**, 2569.

(8) Calderazzo, F.; Poli, R.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1988**, *118*, 595.

(9) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1519.

(10) Kelsey, B. A.; Ellis, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 1344.

(11) Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495.

(12) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1988**, *27*, 99.

(13) Rehder, D.; Müller, I.; Kopf, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1013.

Table II. **θ Angles (deg) for Selected $M(\eta^n\text{-}C_nR_n)L_1L_2L_3L_4$ 17-Electron Piano-Stool Compounds (L_1 Trans to L_3; L_2 Trans to L_4)**

M	C_nR_n	L_1	L_2	L_3	L_4	θ_1	θ_2	θ_3	θ_4	ref
Mo	Cp	Cl	PMe_3	Cl	PMe_3	117.6	113.2	117.2	113.1	2
Mo	Cp*	Cl	PMe_3	Cl	PMe_3	115.4	121.7	113.8	116.6	*a*
Mo	Cp	I	PMe_3	I	PMe_3	117.2	112.7	117.2	106.2	2
Mo	Cp	Cl	PMe_3	I	PMe_3	120.8	108.9	122.0	109.6	*b*
Mo	Cp	Br	Br	dppe		113.7	113.9	110.7	112.1	3
Mo	Cp	Cl	PPh_3	Cl	PPh_3	122.2	109.4	121.8	109.1	*c*

[a] Baker, R. T.; Calabrese, J. C. Unpublished work (structural parameters kindly provided by R. T. Baker). [b] Unpublished results from our laboratory in collaboration with A. L. Rheingold. [c] Unpublished results from our laboratory.

Table III. **θ Angles (deg) for Selected $M(\eta^n\text{-}C_nR_n)L_1L_2L_3L_4$ 16-Electron Piano-Stool Compounds (L_1 Trans to L_3; L_2 Trans to L_4)**

M	C_nR_n	L_1	L_2	L_3	L_4	θ_1	θ_2	θ_3	θ_4	ref
				Type I						
Ti	C_6Me_6	$Cl\text{-}AlCl_2\text{-}Cl$		$Cl\text{-}AlCl_2\text{-}Cl$		115.4	118.8	115.0	119.4	38
Zr	Ar[a]	I	PMe_3	I	PMe_3	128[b]	115[c]			39
				Type II						
Ta	Cp	Cl	Cl	L-L[d]		108.6	111.1			40
Ta	Cp*	Cl	Cl	L-L[e]		105.4	110.6			41
Mo^+	Cp	Cl	PMe_3	Cl	PMe_3	119.1	112.7	117.8	113.8	2
Re	Cp*	Me	Me	Me	Me	107	110	114	114	42[f]
Re	Cp′[g]	X[h]	Y[i]	Cl	Cl	108.5	110.0	115.7	118.5	43[f]

[a] Ar = $\eta^6\text{-}C_7H_7SiMe_3$. [b] Average of θ_1 and θ_3, assuming Ar (center of gravity), Zr, I(1), and I(2) coplanar. [c] Average of θ_2 and θ_4, assuming Ar (center of gravity), Zr, P(1), and P(2) coplanar. [d] L-L = $Me_2CCHCOMe$. [e] L-L = $Me_3SiC(O)P(O)(OMe)_2$. [f] Positional parameters obtained from the Cambridge Crystallographic Database. [g] Cp′ = $\eta^5\text{-}C_5Me_4Et$. [h] X = 75% Cl + 25% CH_3. [i] Y = 25% Cl + 75% CH_3.

Table IV. **θ Angles (deg) for a $M(\eta^n\text{-}C_nR_n)L_1L_2L_3L_4$ 15-Electron Piano-Stool Compound (L_1 Trans to L_3; L_2 Trans to L_4)**

M	C_nR_n	L_1	L_2	L_3	L_4	θ_1	θ_2	θ_3	θ_4	ref
Ta	Cp*	Cl	$SiMe_3$	Cl	PMe_3	114.9	108.9	115.0	123.1	44

Table V. **θ Angles (deg) for Selected $M(\eta^n\text{-}C_nR_n)L_1L_2L_3L_4$ 14-Electron Piano-Stool Compounds (L_1 Trans to L_3; L_2 Trans to L_4)**

M	C_nR_n	L_1	L_2	L_3	L_4	θ_1	θ_2	θ_3	θ_4	ref
Ta	Cp*	$SiMe_3$	Cl	Cl	Cl	109.8	110.4	120.1	110.0	44
Ta	Cp*	Cl	Cl	$CH_2CH_2CH_2CH_2$		116.2	116.2	107.5	107.5	45
Ta	Cp*	Cl	Cl	X-X[a]		115.7	119.3	107.4	108.0	45
Zr	Cp*	Br	Br	$1,2,3\text{-}Me_3C_3H_2$		114.8	114.8			46
Zr	Cp*	Br	Br	$1,1,2\text{-}Me_3C_3H_2$		109.1	110.0			46

[a] X-X = 1,2-dimethylenecyclopentane ($1,2\text{-}c\text{-}C_5H_8(CH_2)_2$).

ported in Table I, 17-electron complexes[2,3] in Table II, 16-electron complexes[2,38-43] in Table III, 15-electron complexes in Table IV,[44] and finally 14-electron complexes in Table V.[44-46] These tables are not comprehensive of all

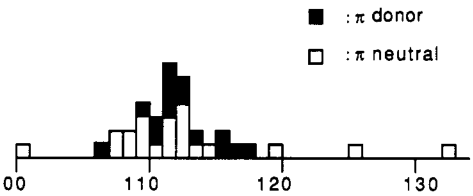

Figure 1. Distribution of θ angles for π-neutral and π-donor ligands in 18-electron compounds.

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(14) Herrmann, W. A.; Kalcher, W.; Biersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558.
(15) Chaiwasie, S.; Fenn, R. H. *Acta Crystallogr.* **1968**, *B24*, 525.
(16) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2202.
(17) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213.
(18) Bird, P. H.; Churchill, M. R. *Inorg. Chem.* **1968**, *7*, 349.
(19) Albright, M. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1978**, *161*, 221.
(20) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1969**, 1309.
(21) Bush, M. A.; Hardy, A. D. U.; Manojlovic-Muir, L.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1971**, 1003.
(22) Hardy, A. D. U.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1900.
(23) Sim, G. A.; Sime, J. G.; Woodhouse, D. I.; Knox, G. R. *Acta Crystallogr.* **1979**, *B35*, 2406.
(24) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953.
(25) Chan, L. Y. Y.; Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1067.
(26) Fenn, R. H.; Cross, J. H. *J. Chem. Soc. A* **1971**, 3312.
(27) (a) Sim, G. A.; Sime, J. G.; Woodhouse, D. I.; Knox, G. R. *Acta Crystallogr.* **1979**, *B35*, 2403. (b) Owens, B. E.; Poli, R. Unpublished work.
(28) (a) Bir'yukov, B. P.; Struchkov, Y. T.; Anisimov, K. N.; Kolobova, N. E.; Bescastnov, A. S. *Chem. Commun.* **1968**, 667. (b) Semion, V. A.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1968**, *9*, 1046.
(29) Denis, J. N. S.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1.
(30) Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8.
(31) Kreissl, F. R.; Wolfgruber, M.; Sieber, W. J.; Ackermann, K. *Organometallics* **1984**, *3*, 777.
(32) Ginzburg, A. G.; Bokyi, N. G.; Yanovsky, A. I.; Struchkov, Y. T.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1977**, *136*, 45.
(33) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.
(34) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301.
(35) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666.
(36) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.
(37) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458.
(38) Thewalt, U.; Österle, F. *J. Organomet. Chem.* **1979**, *172*, 317.
(39) Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 908.
(40) Guggolz, E.; Ziegler, M. L.; Biersack, H.; Herrmann, W. A. *J. Organomet. Chem.* **1980**, *194*, 317.
(41) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1987**, *26*, 2556.
(42) Flöel, M.; Herdtweck, E.; Wagner, W.; Kulpe, J.; Härter, P.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 787.

the four-legged piano-stool structures reported in the literature. We have not included many structures where bridge formation, metal–metal bonding, or other particular geometrical features may introduce a serious perturbation on the θ values. For a few structures described in preliminary communications, we have obtained the structural parameters necessary for the calculations from the Cambridge Crystallographic Database.

In each table, type I compounds are listed first, followed by those of type II. Within each class, compounds are listed according to the metal group number. For the large number (almost all) of the structures where the angles to the ring centroid were not reported, we have calculated them from the cell parameters and atomic coordinates (ring centroid = center of gravity).

1. 18-Electron Compounds. The "Angular Trans Influence". Structural studies on 18-electron compounds have been found for the following classes (Ar = η^6-arene; pd = η^5-pentadienyl; L = neutral two-electron donor; X = anionic two-electron donor or neutral one-electron donor, depending on the formalism used for electron counting): $[V(Ar)L_4]^+$, $[M(Ar)XL_3]^+$ (M = Mo, W), $Mo(Ar)X_2L_2$, $M(pd)L_4$ (M = V, Nb), $M(pd)XL_3$ (M = Mo, W), $[Mn(pd)XL_3]^+$, $Re(pd)X_2L_2$, and $Rh(pd)X_4$. By far, the class that is most represented is $M(pd)XL_3$ for M = Mo and pd = Cp. The crystal structure of $IrCp^*H_4$ has also been reported, but unfortunately no hydride ligand was located.[47]

As can be seen from Table I, π-acceptor ligands have a larger θ value than π-donor or π-neutral ligands. The θ value for π-neutral (H, CH_3, $SnCl_3$, $GePh_3$, etc.) and for π-donor (Cl, Br, I) ligands is typically in the 105–115° range. Occasional deviations from this range may be due to steric effects. Figure 1 shows the distribution of θ angles for π-donor or π-neutral ligands in 18-electron compounds. The large deviations found[37] for $RhCp^*H_2(SiEt_3)_2$ (average 125.9° for the hydride ligands (neutron data) and average 132.6° for the $SiEt_3$ ligands) may have interesting bonding implications (see Discussion). The other large deviation on the small-angle side (100° for the hydride ligand in $[Re(\eta^5\text{-}2,4\text{-}C_5Me_2H_5)H(PMe_2Ph)_3]^+$)[36] has a large uncertainty, the structure having been obtained from an X-ray diffraction experiment. In a couple of instances, that is $[Mo(\eta^6\text{-}C_6Me_6)I(CO)_3]I_5$[8] and *cis*-$MoCpBr(CO)_2(PPh_3)$,[27a] a positional disorder between the halogen and the trans-CO ligand might make the corresponding positional parameters less reliable.

The θ value for CO is typically in the range 115–130°. Its average value increases upon a decrease of the number of CO ligands within the same molecule, although the ranges of values for different classes of derivatives overlap extensively (119–124° for molecules with four CO ligands; 120–125° for molecules with three CO ligands, and 122–128° for molecules with two CO ligands *trans to each other*). For a reason that does not appear obvious to us, CO ligands that are trans to π-donor or π-neutral ligands have a lower θ angle than those trans to other π-acidic ligands.

Figure 2 shows the distribution of average θ angles for CO ligands that are trans to each other as opposed to CO ligands trans to other ligands. The effect can be either small (such as in $MoCp(AuPPh_3)(CO)_3$: 123.2° for CO trans to $AuPPh_3$ vs 125.0 and 125.4° for the two CO ligands trans to each other)[30] or large (such as in $WCpCl(CO)_3$: 111.7° for the CO trans to Cl vs 125.1 and 125.7° for the other CO ligands),[16] but it is always present. Notice also the low θ angles for CO in *cis*-$MoCpI(PBu_3)(CO)_2$, *cis*-$MoCpBr(PPh_3)(CO)_2$, and *cis*-$ReCp^*I_2(CO)_2$, compared with those in analogous trans compounds. This behavior is very consistent for the structures assembled in Table I and can be considered to have general validity. Throughout the paper, we will refer to this effect as "angular trans influence", since it is a thermodynamic effect and is dependent on the nature of the trans ligand. It differs substantially, however, from the better known trans influence for octahedral and square-planar coordination compounds because it deals with bond angles rather than with bond lengths.

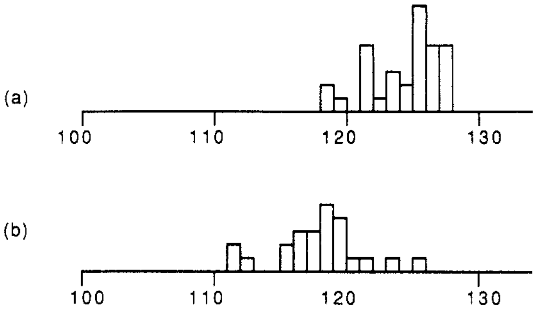

Figure 2. Distribution of θ angles for CO in 18-electron compounds: (a) trans to CO; (b) trans to other ligands.

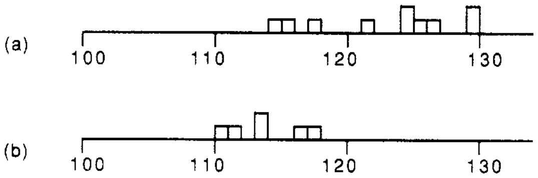

Figure 3. Distribution of θ angles for phosphine and phosphite ligands in 18-electron compounds: (a) trans to CO or other phosphine; (b) trans to non-π-acidic ligands.

Phosphine ligands tend to have large θ angles. Striking examples are *trans*-$ReCpH_2(PPh_3)_2$ (average 125.7°),[34] *trans*-$[ReCpH(MeCN)(PPh_3)_2]^+$ (average 124.4°),[35] the two trans-phosphine ligands in $[Re(2,4\text{-}C_5H_5Me_2)H(PMe_2Ph)_3]^+$ (average 126.8°),[36] and especially *trans*-$Mo(\eta^6\text{-arene})Me_2(PPhMe_2)_2$ (arene = benzene, toluene; average 129.7 and 129.8°, respectively).[9] Like CO, phosphine ligands experience an angular trans influence: phosphines that are trans to CO or to another phosphine tend to have larger θ angles than phosphines that are trans to π-neutral or π-donor ligands (see Figure 3). The most notable examples are $MoCpCl(dppe)(CO)$,[21] with 124.8° for the phosphorus atom trans to CO and 110.2° for the phosphorus atom trans to the chlorine atom, and $[Re(2,4\text{-}C_5H_5Me_2)H(PMe_2Ph)_3]^+$,[35] with 126.8° (average) for the phosphine ligands trans to each other and 113.7° for the phosphine trans to the hydride ligand.

There does not appear to be an angular trans influence on the θ angle to π-neutral or π-donor ligands, indicating that the probable cause of this effect lies in the π interactions.

2. 17-Electron Compounds. Most of the structural work on four-legged piano-stool compounds with a 17-electron count comes from our own research. The structural data, which are all related to Mo(III) compounds of formula $Mo(pd)X_2L_2$, are assembled in Table II. All the compounds reported, except for $MoCpBr_2(dppe)$, have a

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(43) Herrmann, W. A.; Felixberger, J. K.; Herdtweck, E.; Schafer, A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 466.

(44) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037.

(45) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3112.

(46) Larson, E. J.; Van Dort, P. C.; Dailey, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Organometallics* **1987**, *6*, 2141.

(47) Gilbert, T. M.; Bergman, R. G. *Organometallics* **1983**, *2*, 1458.

trans arrangement of the neutral donors.

None of the compounds reported contains ligands that can be considered π neutral. The π-donor ligands, in contrast with the 18-electron compounds discussed above, have a *larger* θ angle than the phosphine ligands for almost all the entries of Table II, the $MoCp^*Cl_2(PMe_3)_2$ compound being the only exception. In the latter compound, the large angle of the phosphine ligands is probably caused by a steric interaction with the methyl groups of the Cp* ring. The other structures have angles to the phosphines in the narrow 109–113° range, which is considerably less than the range found for trans phosphines in 18-electron compounds (vide supra).

The θ angles to the halide ligands are in the 113–122° range. It is interesting to observe that the electronically richest system, i.e. $MoCp^*Cl_2(PMe_3)_2$, has the smallest of such angles, whereas the electronically poorest system, i.e. $MoCpCl_2(PPh_3)_2$, has the largest.

3. 16-Electron Compounds. A diverse, although not extensive, set of structures is available for 16-electron compounds. π-neutral ligands are present in $ReCp^*Me_4$[42] and in $Re(\eta^5\text{-}C_5Me_4Et)MeCl_3$.[43] Although in neither of these structures are the θ values very accurate because of disorder problems, they compare well with those found in 18-electron complexes. π-donor ligands are represented in $Ti(C_6Me_6)(\mu,\mu'\text{-}Cl_2AlCl_2)_2$ (average $\theta = 117.1°$),[38] in the above-mentioned $Re(\eta^5\text{-}C_5Me_4Et)MeCl_3$ compound (average $\theta = 117.1°$ for the two nondisordered chloride ligands),[43] in two *cis*-$TaCpCl_2(L\text{-}L)$ structures (average $\theta = 108.2°$),[40,41] and in two *trans*-MX_2L_2 structures, i.e. the high-spin $[MoCpCl_2(PMe_3)_2]^+$ cation (average $\theta = 118.4°$)[2] and the low-spin $Zr(\eta^6\text{-}C_7H_7SiMe_3)I_2(PMe_3)_2$ compound (average $\theta = 128°$).[39] Thus, the θ angle for potential π donors varies over a quite large range, the lower limit being comparable to the values observed in 18-electron compounds. Of special notice is the large angle for the iodo ligands in the zirconium compounds, which corresponds to a trans I–Zr–I angle of only 104°.

Ligands that are potential π acceptors (PMe_3) are present in only two of the compounds investigated, that is $[MoCpCl_2(PMe_3)_2]^+$ and $Zr(\eta^6\text{-}C_7H_7SiMe_3)I_2(PMe_3)_2$.[2,39] For both compounds, the θ values are in the same range observed for 17-electron compounds and are lower than those of 18-electron compounds.[56] The formally neutral bidentate ligands $Me_2C{=}CHC(O)Me$[40] and $Me_3SiC(O)P(O)(OMe)_2$[41] are also π acceptors, as evidenced by their side-on η^4 coordination, but the θ angles corresponding to them cannot be calculated without ambiguity.

4. 15- and 14-Electron Compounds. Only one 15-electron compound has been structurally characterized to the best of our knowledge. This is the tantalum(IV) compound $TaCp^*(SiMe_3)Cl_2(PMe_3)$ with the two chloro ligands trans to each other. The π-neutral $SiMe_3$ group has a θ angle of 108.9°. The two chloro ligands have θ angles of 114.9 and 115.0°, respectively, and the PMe_3 ligand has an angle of 123.1°. In analogy to the 17-electron $MoCp^*Cl_2(PMe_3)_2$ compound discussed above, the PMe_3 ligand in this 15-electron tantalum compound might experience a steric interaction with the Cp* ligand, which might be, at least in part, responsible for the large θ angle. However, the $SiMe_3$ ligand that is present in the same system is similar in size to the PMe_3 ligand and exhibits a much smaller θ angle.

A handful of type I 14-electron compounds have been structurally characterized. π-neutral ligands ($SiMe_3$, alkyls) have θ angles in the range 107–110°, i.e. similar to what is found for the same ligands in 15-, 16-, and 18-electron compounds. The π-donor ligands (Cl, Br) have higher angles, in the range 109–120°. The only potential π-acceptor present in these structures is the allyl system, for which the calculation of θ is not straightforward.

Discussion

For 18-electron compounds, both the z^2-based and the xy-based orbitals contain two electrons. In this case, the θ angle is not anticipated to be sensitive to the presence of filled π orbitals on the ligand (potential π-donor ligand) because both the π-bonding orbitals (mainly constituted by the ligand lone pairs) and π-antibonding orbitals (HOMO and SHOMO) are full. In fact, Table I and Figure 1 show that π-donor and π-neutral ligands have θ angles in the same range. Since there are no π effects on these ligands, we might take their observed average θ (ca. 110°) as the reference "undistorted" value. A notable deviation from this value is observed for both the hydride (average 132.6°) and the triethylsilyl (125.9°) ligands in the compound $RhCp^*H_2(SiEt_3)_2$.[37] A steric interaction between the silyl ethyl groups and the Cp* methyl groups could be, at least in part, responsible for the increase of θ for $SiEt_3$, but this argument does not hold for the smaller hydrido ligands. The structure comes from neutron data, so there is no question about the precision of the hydride positional parameters. Koetzle, Maitlis, and co-workers describe the structure as possessing five formally uninegative ligands (the intramolecular distances $H\cdots H = 2.328\ (4)$ Å and $Si\cdots H = 2.27\ (6)$ Å (average) show no significant bonding interaction). On the basis of the large deviation of the θ angles from the normal range for π-neutral ligands, we suggest that the structure lies on the reaction coordinate for reductive elimination of Et_3SiH, although very close to the product of complete oxidative addition.[57]

For potential π-acceptor ligands, both the HOMO and the SHOMO can exert their full π-back-bonding capability in 18-electron compounds. Since these two orbitals have an opposite tendency to distort bonds to π acids as discussed above (z^2 tends to increase the θ value, whereas xy tends to decrease it), and since the observed θ values for π acids are *greater* than for π-donor or π-neutral ligands, it would appear that π back-donation from the z^2 orbital is stronger. In other words, the metal z^2 orbital is the better π donor. An orientation analysis for single-faced π acceptors[1] has suggested, however, that the ligands will orient in such a way as to accept electron density from the metal xy orbital. It is not easy to reconcile these two observations. Certainly, better π back-donation from z^2 seems reasonable on the basis of a better energy match between the donor and acceptor orbitals. We simply observe that the preference for a particular π-donor orbital (z^2 or xy) might strongly depend on the nature of the other ligands on the metal, especially the one in the trans position, as also suggested by the data in Table I.

The θ angle for CO *increases* with the degree of π back-donation from the transition metal, again in agreement with a better π donation from z^2. For instance, the average θ angle for $[TiCp(CO)_4]^-$ (123.7°) is greater than the same average for $VCp(CO)_4$ (118.7°). The better π-donating ability to Ti(0) with respect to that of V(I) is indicated by the lower CO stretching frequencies for the titanium compound (1923, 1781 cm^{-1} in dimethoxyethane)[10] with respect to those of the vanadium analogue (1982, 1890 cm^{-1} in CS_2).[48] However, infrared spectroscopy indicates that V(I) is a better π base than Nb(I) (CO stretching vibrations for $NbCp(CO)_4$ are at 2029, 1933 cm^{-1} in pentane),[14] whereas the average θ angle is slightly larger

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(48) King, R. B. *Organometallic Syntheses*: Academic Press: New York, 1965; Vol. 1, p 105.

for the niobium compound (121.0°). The general increase of the average θ as the number of CO ligands decreases is also consistent with a direct relationship between the θ angle and the extent of π back-bonding.

Phosphine ligands usually have large θ values, sometimes comparable to those observed for the CO ligands, especially in those compounds where the trans ligand is CO or another phosphine (see "angular trans influence" in the Results). Thus, the data suggest that phosphine ligands are good π acceptors in these systems. Steric effects might be the cause of high θ angles for the phosphine ligands in compounds where the "stool" ligand is extensively substituted, e.g. Cp* and 2,4-dimethylpentadienyl. However, the large angles found in compounds with unsubstituted Cp or arene do not appear to be the result of steric effects. For instance, in the *trans*-$Mo(\eta^6\text{-}C_6H_6)Me_2(PMe_2Ph)_2$ compound, the angle between the bonds to η^6-benzene (cone angle 143.4°)[49] and to PMe_2Ph (cone angle 122°)[50] averages 129.7° (only 3° smaller than the average cone angle of the two ligands), compared with 100.6° between the bonds to the two trans phosphines (21.4° smaller than the phosphine cone angle). Therefore, the two phosphine ligands experience a larger compression against each other than against the arene ligand. A comparison of the phosphine θ angles in 18-electron compounds with those in 17- and 16-electron compounds (vide infra) also suggests that these deviations are mainly caused by electronic effects. Alternative evidence, based on bond distances rather than angles, that phosphine ligands (e.g. PMe_3, dppe) are π acceptors in monocyclopentadienyl compounds of Mo(III) is available from our previous work.[2]

The phenyl group's angle in $WCpPh(CO)_3$ (119.1 and 116.6° for the two independent molecules in the asymmetric unit) is slightly higher than the typical one for π-neutral ligands. Since the phenyl group has orbitals suitable to accept electron density from the metal in a π fashion, it is natural to ask the question whether any π back-bonding is present here. The problem of π back-donation to aryl ligands has not been extensively addressed. Measurements of rotational barriers around the metal–aryl bond in Rh(III) and W(III) compounds point toward little or no back-bonding in those systems.[51] The $GaMe_2$ ligand in $WCp(GaMe_2)(CO)_3$ is also a potential π acceptor. The geometry around the gallium atom is perfectly planar, indicating sp^2 hybridization and leaving the remaining empty p orbital available to receive electron density from the metal. However, the $WGaMe_2$ plane is parallel to the GaW-*trans*-CO plane, making the overlap of the empty p orbital possible only with the metal xy orbital in analogy with the case for the carbene derivative $MoCp(GePh_3)(CO)_2(C(OEt)Ph)$[25] and the model $[MoCp(PH_3)(CO)_2(CH_2)]^+$ system examined by Hoffmann.[1] The observed θ value is 117.5°, whereas, according to our model, electronic effects would tend to predict a smaller θ value for this ligand given its orientation. It may be that the steric interaction between the endo-CH_3 of the $GaMe_2$ ligand and the Cp group keeps the θ angle higher than its optimum value.

The θ value of 118.3° observed for the tetrahydrothiophene ligand in $VCp(tht)(CO)_3$ would tend to suggest some degree of π back-donation to the sulfur-based ligand. π back-bonding to sulfur ligands is a topic of controversy. It would be valuable in this respect to obtain a crystal structure for a $VCpL(CO)_3$ compound where L is a neutral oxygen- or nitrogen-based ligand (e.g. THF, MeCN, etc.). To the best of our knowledge these compounds have not been isolated in crystalline form.[52,53] The θ angles of other ligands reported in Table I follow the expected trends on the basis of what was discussed above.

For 17-electron compounds (Table II), the HOMO (i.e. the metal z^2-based orbital) is only half-occupied. As predicted on the basis of the model described above, the θ angle of π donors increases with respect to the typical angle found in 18-electron compounds (e.g. around 110°). The angle becomes as large as 122° in *trans*-$MoCpCl_2(PPh_3)_2$ and *trans*-$MoCpICl(PMe_3)_2$. It should be noted that the steric interactions with the two bulky PPh_3 ligands tend to decrease, not increase, the value of the angle θ for the chloride ligands. The same might be said of the two trans iodide ligands in $MoCpI_2(PMe_3)_2$, which form an I–Mo–I angle of 125.6°, compared with similar trans X–M–X angles in 18-electron compounds in the 138–142° range. Thus, what we are seeing here is clearly an electronic effect. This effect shows, if the model is correct, that ligands such as Cl^- and I^- *are indeed* π *donors* in this system. This conclusion is in accord with the result of Fenske–Hall MO calculations on the model $MoCpX_2(PH_3)_2$ compounds.[2]

The θ angles for the phosphine ligands are significantly lower than those found for corresponding 18-electron compounds. This is again in agreement with the model and with the idea that phosphine ligands, even PMe_3,[2] *are indeed* π *acceptors* in these systems. For $MoCpCl_2(PPh_3)_2$ the bulky phosphine ligands (cone angle 145°)[50] are very close to the Cp ligand (cone angle 140.4°):[49] the average θ value is 109.2°, i.e. 33.5° smaller than the average cone angle of the two ligands. On the other hand, the two PPh_3 ligands form a P–Mo–P angle of 141.7°, only 3.3° smaller than the phosphine cone angle. Thus, in this compound the two phosphine ligands are compressed against the Cp ligand much more than they are to each other, in a fashion perfectly opposite to that for the 18-electron Mo(arene)$Me_2(PMe_2Ph)_2$ systems (vide supra).

The increase of θ for π donors continues when the electron count decreases further to 16. Because of the above-mentioned "angular trans influence", we should compare only those systems with the same number and type of π acceptors and π donors in the same relative configuration. For instance, let us compare the 16-electron $Zr(\eta^6\text{-}C_7H_7SiMe_3)I_2(PMe_3)_2$[39] (average θ angles: I, 128°; PMe_3, 115°) with the 17-electron $MoCpI_2(PMe_3)_2$[2] (I, 117.2°; PMe_3, 109.4°). There are no 18-electron systems of formula $M(\pi\text{-ligand})X_2(PR_3)_2$ with two phosphines and two π-donor ligands and, at least for the case M = Mo and π-ligand = Cp, an argument for their nonexistence has been produced.[2] However, we have seen earlier that π-donor and π-neutral ligands have similar θ angles in 18-electron compounds (Figure 1), and a few 18-electron compounds with two trans phosphines and two trans π-neutral ligands exist: $Mo(\eta^6\text{-}C_6H_6)Me_2(PMe_2Ph)_2$[9] (Me, 109.6°; PMe_2Ph, 129.7°) and $ReCpH_2(PPh_3)_2$[34] (H, 111°; PPh_3, 125.7°). This comparison also shows that the large drop for the phosphine's θ angle occurs on going from the 18- to the 17-electron count. No further decrease (in fact, a slight increase) is observed on going from 17 to 16 electrons, as predicted by the model (we should point out here that the 16-electron zirconium compound has a low-spin configuration).[39] This probably happens because even the smallest phosphine ligands could not decrease their

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(49) Calculated from the observed Mo–centroid distance, C–C = 1.395 Å, C–H = 1.08 Å, and a van der Waals radius of 1.2 Å for H.

(50) Tolman, C. A. *Chem. Rev.* 1977, *77*, 313.

(51) (a) Jones, W. D.; Feher, F. J. *Inorg. Chem.* 1984, *23*, 2376. (b) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffmam, J. C. *Organometallics* 1989, *8*, 49.

(52) Hoch, M.; Rehder, D. *J. Organomet. Chem.* 1985, *288*, C25.

(53) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* 1978, *100*, 7902.

θ angle much below their observed value in 17-electron compounds without introducing a substantial steric strain in the system. However, more examples of low-spin 16-electron structures with two trans phosphines and two trans halides will be necessary before this analysis can be more meaningful.[56] Another 16-electron structure containing two trans phosphines and two trans halides, that is $[MoCpCl_2(PMe_3)_2]^+$, is known.[2] However, this system has a high-spin configuration. The average θ angles of both Cl and PMe_3 are almost identical with those in the parent 17-electron $MoCpCl_2(PMe_3)_2$ molecule,[2] suggesting that the effect of removing one electron from the xy orbital is small, much smaller than the effect of removing one electron from the z^2 orbital. Again, more structures are needed to assess this point in a more conclusive fashion.

Too few structures of 15- and 14-electron systems are available to draw meaningful conclusions. The only molecule containing a phosphine ligand is the 15-electron $TaCp^*(SiMe_3)Cl_2(PMe_3)$, with a θ angle of 123.1°.[44] This angle appears too large, since only one electron in the xy orbital is available for π back-bonding. As pointed out in the Results, the steric interaction with the bulky Cp* ligand might be responsible for this distortion. The angles of π-neutral ligands are in the same range observed for 18-electron systems, in perfect agreement with the considerations made in the description of the model. π donors exhibit angles, on the average, slightly greater than those observed for the same ligands in 18-electron compounds, indicating that π donation into the z^2 orbital might be slightly more important. However, the high dispersion of these values and the limited number of structures with this type of ligand prevent a more detailed analysis from being carried out. With respect to this point, it would be of greate help to analyze the structure of a 14-electron compound where at least one of the ligands is a single-faced π donor (e.g. NR_2). Structures of this type, however, are not yet available.

A final remark concerns the description, often found in the chemical literature, of mononegative tris-chelating ligands such as hydrotris(pyrazolyl)borate ($HB(pz)_3$) as cyclopentadienyl analogues. The analogy between these two systems is justified in that they donate the same number of electrons, they occupy three mutually cis coordination positions (at least in a formal sense for Cp), and their steric bulk can be modified in the same way through methyl substitution. However, there is no possibility for the borate ligand to accept metal electron density via δ back-bonding. In fact, the structure of $(HB(pz)_3)TaMe_4$,[54] which is isoelectronic with $TaCp^*(SiMe_3)Cl_3$ and $TaCp^*Cl_2(CH_2CH_2CH_2CH_2)$, is pseudo tbp if we consider the pyrazolylborate as occupying a single coordination position (capped octahedral when the pyrazolylborate is considered as occupying three mutually cis coordination positions). This corresponds to a coordination geometry that is yet to be found for the cyclopentadienyl analogues.

Conclusions

Our analysis of existing four-legged piano-stool structures of types I and II shows that the value of the angle θ between a monodentate ligand and the center of gravity of the π-bonded aromatic ligand depends on the electronic structure of the complex (electron count) and on the π-bonding capabilities of the ligand (e.g. whether the ligand is a π-donor, π-acceptor, or π-neutral ligand). A simple set of rules predicts correctly the trend of the θ angle as the metal electron count changes. The analysis shows that the metal z^2 orbital (HOMO) is a better π donor than the xy orbital (SHOMO). It also shows that phosphine ligands are good π acids in at least some of the structures analyzed and that halide ligands are involved in π donation in those compounds where the metal has less than 18 electrons in the valence shell. By use of the results of this analysis, a correlation between the experimental θ angle and the π-bonding ability of a ligand or metal is possible. Finally, any major deviation from the expected range of θ values can be taken as an indication of "unusual" bonding characteristics. This has been the case for $RhCp^*H_2(SiEt_3)_2$, for which the description as the product of an "arrested" oxidative addition of Et_3SiH to the rhodium center is proposed, and for $[IrCpH_3(PMe_3)]^+$.[57]

In addition, our analysis has uncovered an "angular trans influence" on the value of the angle θ, which is most evident for π-acidic ligands (CO, phosphines). A perceptive reviewer suggests a way to interpret this effect. His/her argument is based on the observation that, in most cases, the θ angles distort in such a way that the two larger angles correspond to trans ligands, as also do the two smaller angles. This also happens in a few cases where one of the ligands with the large θ angle is not a π-acidic one, such as for *cis*-$MoCpBr(CO)_2(PPh_3)$[27a] and *cis*-$ReCp^*I_2(CO)_2$[33] (see Table I). Considering the geometry as pseudo square pyramidal, the distortions are along the well-known Berry pseudorotation coordinate, which interconverts sp and tbp structures. The ring and the two ligands with the largest θ values become the equatorial ligands, and the two ligands with the smaller θ values become the axial ligands. There are only two possible distortions of the sp geometry to the tbp geometry, corresponding to the two different sets of trans ligands to bend down. The set that does bend down is presumably the one with the best "net" π-accepting capability. This argument would appear to be consistent with the well-known rule that in tbp complexes the best π-accepting ligands are found in equatorial positions.[55]

This interpretation has some appeal but is both phenomenologically and theoretically too simplistic. First, a distortion along the Berry pseudorotation coordinate is not always observed. In such cases as $MCp(CO)_4$ (M = V, Nb) and $TiCp(CO)_4^-$, both pairs of trans ligands distort in the same direction, i.e. toward larger θ values. Second, in several cases where the angular trans effect is noticeable, e.g. the $M(pd)X(CO)_3$ compounds, the CO trans to X deviates toward angles smaller than those attained by the two CO's trans to each other but *still larger* than the ideal value for the sp geometry, in contrast to what is expected on the basis of the Berry pseudorotation distortion. Third, we must point to the fact that the electronic structure of

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(54) Reger, D. L.; Swift, C. A.; Lebioda, L. *Inorg. Chem.* **1984**, *23*, 349.

(55) (a) Schreiner, A. F.; Brown, T. L. *J. Am. Chem. Soc.* **1968**, *90*, 3366. (b) Udovich, C. A.; Clark, R. J.; Haas, H. *Inorg. Chem.* **1969**, *8*, 1066. (c) Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 1970. (d) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(56) Note Added in Proof: The structures of the 16-electron compounds $WCp(CO)(SC_6F_5)_3$ and $[MoCp(SC_6F_5)_4]^-$ (both low-spin systems) have appeared: Abu Bakar, W. A. W.; Davidson, J. L.; Lindsell, E. W.; McCullogh, K. J. *J. Chem. Soc., Dalton Trans.* **1990**, 61. The authors analyze the structural parameters of $WCp(CO)(SC_6F_5)_3$ on the basis of the same MO model presented here. In particular, the θ angle for CO is only 102.6°. The thiolate ligand that is trans to CO has an angle of 110.2°, whereas the two other thiolates (trans to each other) have an average angle of 119.9°. This shows that the angular trans influence is not restricted to 18-electron systems. In the second compound, all four thiolates have θ angles in the range 109–113°.

(57) Note Added in Proof: A similar situation is found for the recently reported neutron diffraction structure of $[IrCpH_3(PMe_3)]^+$: Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. θ angles are as follows: Cp–Ir–P = 131.7 (2)°; $Cp–Ir–H_t$ = 130.0 (4)°; $Cp–Ir–H_c$ = 123.0 (4) and 120.6 (4)°. These data strongly support the conclusion of Heinekey and co-workers, which was primarily based on NMR data, that there must be some kind of interaction between the three hydride ligands.

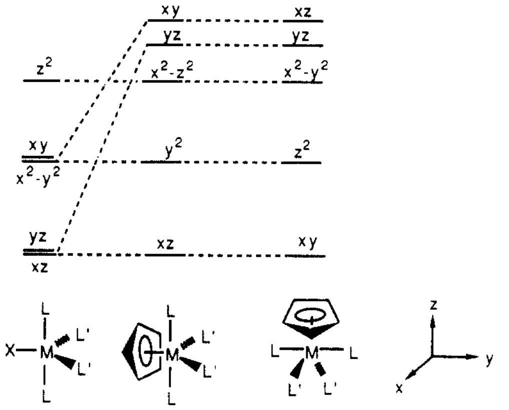

Figure 4. Qualitative relationship between the metal d orbitals in a tbp coordination compound and in pseudo tbp structure where one of the equatorial ligands is a six-electron-donor aromatic ring (the diagram is identical for ring = arene, Cp (shown), or cyclobutadiene).

a tbp complex is drastically changed when a six-electron donor such as Cp or an arene occupies one equatorial position. Looking at these two limiting geometries as tbp and sp is geometrically reasonable but electronically unacceptable. One of the two orbitals that is responsible for making the equatorial positions in the tbp structure better for π acceptors (xy) is sequestered by the π interaction with the organic ring and so is another orbital (yz) (see Figure 4, left and middle diagrams). Upon proper reorientation of the axes, the right-hand diagram is obtained, which presents the same relative ordering of the ideal four-legged piano stool, as expected.

Figure 4 allows one to rationalize (on the basis of the better π-donation properties of the z^2 orbital) why, in a 18-electron structure with two trans π donors and two trans π acceptors, the π donors will prefer the positions with the smaller θ (pseudoaxial position in the tbp description) and the π acceptors will prefer the positions with the larger θ, whereas the reverse is true for 17-electron and low-spin 16-electron complexes, but it failes to explain why a π acid will have a larger θ value when trans to another π acid with respect to when it is trans to another non-π-acidic ligand *within the same structure*, as for instance in MoCp(C_3F_7)$(CO)_3$. A more in-depth analysis of the electronic structure seems to be necessary to explain this effect.

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O-Protonation of the $(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}$ Anion. Rearrangement of $(\mu\text{-H})Ru_3(\mu\text{-COH})(CO)_{10}$ to $H(\mu\text{-H})Ru_3(CO)_{11}$. Kinetics of Reductive Elimination of Hydrogen from $H(\mu\text{-H})Ru_3(CO)_{11}$

Leigh R. Nevinger and Jerome B. Keister*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

John Maher*

School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

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The kinetic product from protonation of $[(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}]^-$ with CF_3SO_3H is $(\mu\text{-H})Ru_3(\mu\text{-COH})(CO)_{10}$. This product rearranges to $H(\mu\text{-H})Ru_3(CO)_{11}$ within 20 s at 25 °C. Alternatively, $H(\mu\text{-H})Ru_3(CO)_{11}$ is the only product formed by protonation with CF_3CO_2H. Products were characterized by ^1H NMR spectroscopy at low temperatures and by FT-IR spectroscopy at ambient temperature. $H(\mu\text{-H})Ru_3(CO)_{11}$ is isostructural with the Os analogue, having one bridging and one terminal hydride ligand; these hydrides undergo exchange on the NMR time scale ($\Delta G^* = 51.9$ kJ/mol at 236 K). $H(\mu\text{-H})Ru_3(CO)_{11}$ decomposes rapidly (k(298 K) = $(1.27 \pm 0.19) \times 10^{-2}\ s^{-1}$) to $Ru_3(CO)_{12}$ and hydrogen. Activation parameters ($\Delta H^* = 124$ (6) kJ/mol, $\Delta S^* = 136$ (20) J/(K mol)) and the deuterium kinetic isotope effect ($k_H/k_D = 1.12$ (0.09) at 298 K) were determined by using stopped-flow FT-IR spectroscopy.

Introduction

Transition-metal complexes of the hydroxycarbyne ligand (COH), although generally unstable with respect to the tautomeric hydrido carbonyl complexes, are possible intermediates in carbon monoxide reduction.[1] Complexes of doubly bridging,[2] triply bridging,[3] and quadruply bridging[4] COH ligands are known, in all cases formed by O-protonation of metal carbonyl anions.

O-Protonation of a carbonyl ligand was first reported in 1978, when $(\mu\text{-H})Fe_3(\mu\text{-COH})(CO)_{10}$ was identified by NMR spectroscopy as the product from anhydrous protonation of $[(\mu\text{-H})Fe_3(\mu\text{-CO})(CO)_{10}]^-$ at low temperatures.[5] Protonation of the analogous osmium anion at room temperature forms the unusual cluster $H(\mu\text{-H})Os_3(CO)_{11}$,

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[1] Nicholas, K. M. *Organometallics* **1982**, *1*, 1713.

[2] Hodali, H. A.; Shriver, D. F. *Inorg. Chem.* **1979**, *18*, 1236.

[3] (a) Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1979**, 397. (b) Adams, H.-N.; Fachinetti, G.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 125.

[4] Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 6754.

[5] Hodali, H. A.; Shriver, D. F.; Ammlung, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5239.

0276-7333/90/2309-1900$02.50/0