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Axial Bonding Capabilities of Square Planar d^8-ML_4 Complexes. Theoretical Study and Structural Correlations

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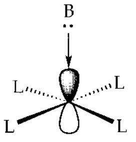
A qualitative molecular orbital study and a structural analysis of the bonding capabilities of the metal atoms in square planar ML_4 complexes of d^8 ions are presented. In addition to analyzing the donor−acceptor properties of the metal atom in such complexes, the following aspects are also studied: (a) the effect of axial groups (bases or acids) on the donor−acceptor properties of the metal atom; (b) the effect of the axial groups on the deviation of the ML_4 ensemble from planarity; (c) the effect of an axial group on the bond between the metal atom and another group in *trans*; and (d) the implications on chemical reactivity.

The square planar complexes of d^8 transition metal ions comply with the 16 electron rule and can in general be isolated as stable species. Ligand substitution reactions or isomerization reactions usually proceed with retention of the square planar stereochemistry. Yet, these compounds have two nonbonding valence orbitals in the exposed region perpendicular to the molecular plane: the occupied d_{z^2} and the empty p_z orbitals. The first one makes the metal atom a potential electron donor toward a Lewis acid, whereas the latter can act as an acceptor toward a Lewis base (**1**). Moreover, the metal atom in such complexes could simultaneously bind a base and an acid to its two available axial coordination sites.



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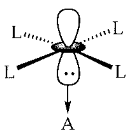

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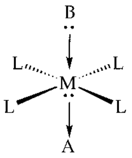

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The simple orbital picture outlined above will be carried on in this paper by the use of qualitative molecular orbital theory, based on extended Hückel calculations, and will allow us to present a systematic approach to a large amount of experimental information and deduce some structural correlations. The orbital nature of the donor properties of the metal atoms in square planar complexes was early recognized by Balch and coworkers,[1−3] and detailed theoretical studies have been devoted to the Tl···Pt interaction in the $Tl_2[Pt(CN)_4]$ compound.[4] Nevertheless, we intend to provide a simple description of the orbital interactions involved in several aspects of the chemistry and structure of square planar complexes, some of which have not been investigated before, and to provide a thorough analysis of the related structural data. Aspects to be treated in this paper are (a) the effect of axial groups (bases or acids) on the donor/acceptor properties of the metal atom, (b) the effect of the axial groups on the deviation of the ML_4 ensemble from planarity, (c) the effect of an axial group on the bond of another group to the metal atom, and (d) the implications on chemical reactivity.

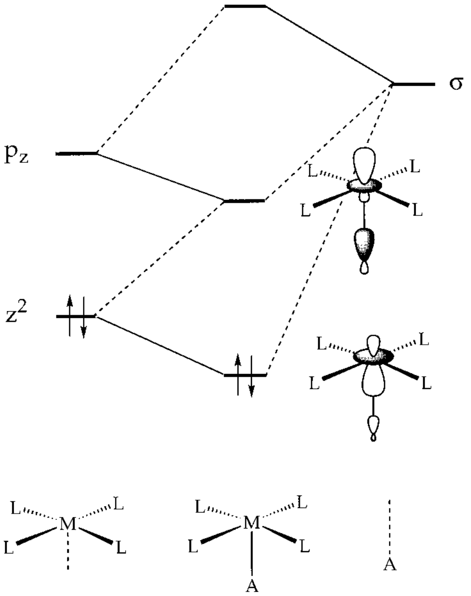

Figure 1. Schematic diagram for the σ-type orbital interaction between a square planar d^8-ML_4 complex and a Lewis acid A along the axial direction.

Molecular Orbital Study

d^8-ML_4 Complexes as Donors. In our EH calculations, the interaction of a model ML_4 complex, $[RhCl_4]^{3-}$, with a Lewis acid (A = H^+, Na^+, or AuCl) in an axial coordination site appears to be clearly stabilizing. Such stability can be attributed to the overlap between the empty valence orbital of the incoming group and the d_{z^2} orbital of the metal atom, as schematically shown in Figure 1. The calculated binding energies, given only as a semiquantitative indication of the strength of the different interactions, increase in the order $Na^+ < AuCl < H^+$ (0.1, 0.5, and 5.5 eV, respectively), as the covalency of the Rh−A bond increases. Such orbital interaction is in keeping with the existence of a wide variety of adducts of ML_4 complexes with a Lewis acid occupying an axial position (see Table 1 and discussion below), formally 16 electron species.

Given the existence of an empty p_z orbital at the metal atom, the bonding molecular orbital (essentially d_{z^2}) is hybridized

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Table 1. Structural Data for Adducts of d^8-ML_4 Complexes with Lewis Acids (*AML_4*, *$A\{ML_4\}_2$*, and *A_2ML_4*)[a]

compound	M	A	M−A (Å)	α_A (deg)	compound	M	A	M−A (Å)	α_A (deg)
AML_4									
$[RhCu(Me_2N_3)(PPh_3)_2(CO)Cl]$	Rh	Cu	2.738	91.8	$[\{PtPd(mec)_2(MeNH_2)_2\}_2(pyz)]^{2+}$	Pt	Pd	2.492	89.3
$[Rh_2(dppm)_2(O_2C_6Cl_4)(CO)]$	Rh	Rh	2.637	92.5	$[PtPd(mec)_2(NH_3)_3]^{2+}$	Pt	Pd	2.511	89.1
$[Rh_2(etdp)_2Cl_2(CO)]$	Rh	Rh	2.661	91.5	$[PtPd(mec)_2(NH_3)_2(meu)]^{+}$	Pt	Pd	2.515	89.6
$[Rh_2(pnp)_2(CO)]^{2+}$	Rh	Rh	2.674	90.9	$[PtPd(mec)_2(NH_3)_2Cl]^{+}$	Pt	Pd	2.518	89.8
$[Rh_2(tdpm)(MeCN)_2(CO)_2]^{2+}$	Rh	Rh	2.745	90.1	$[PtPd(mec)_2(MeNH_2)_2(SCN)]^{+}$	Pt	Pd	2.521	89.4
$[Rh_2Ag(PPh_3)(C_6F_5)_2(P\{OPh\}_3)]$	Rh	Ag	2.635	90.4	$[PtAg(C_6F_5)_3(tht)(PPh_3)]$	Pt	Ag	2.637	92.9
$[Rh(oep)][In(oep)]$	Rh	In	2.584	89.9	$[PtAg(C_6F_5)_4(tht)]^{-}$	Pt	Ag	2.641	92.6
$[RhAu(pnp)_2]^{2+}$	Rh	Au	2.850	89.5	$[PtAg(C_6F_5)_2(C_6Cl_5)(tht)(PPh_3)]$	Pt	Ag	2.650	93.5
$[RhAu(pnp)_2]^{2+}$	Rh	Au	2.857	89.9	$[PtAg(C_6F_5)_2(C_6Cl_5)_2(tht)]^{-}$	Pt	Ag	2.692	91.3
$[Pd_2Na_2(mtc)_6(Hmtc)_2]$	Pd	Na	3.101	91.8	$[PtCl_2\{PtAg(C_6F_5)_3(tht)(PhMe)\}_2]$	Pt	Ag	2.818	92.1
$[PdTl(MeCO_2)_5]$	Pd	Tl	2.702	90.9	$[PtAg(Hmec)(meu)(NH_3)_2]^{2+}$	Pt	Ag	2.906	90.2
$[PdTl(crown)(CN)_2]^{+}$	Pd	Tl	2.897	92.4	$[Pt_2Me_3(dppm)_2]^{+}$	Pt	Pt	2.769	92.4
$[IrCu(Me_2N_3)(Me_2PPh)_2(CO)Cl]$	Ir	Cu	2.686	90.7	$[PtAu(dppm)_2(CN)_2]^{+}$	Pt	Au	3.046	91.3
$[IrCu(dppm)_2(CO)(CCPh)Cl]$	Ir	Cu	2.832	90.7	$[PtHg(Me\text{-}mec)_2(MeNH_2)_2]^{2+}$	Pt	Hg	2.765	89.7
$[IrAu(dppe)_2(PPh_3)]^{2+}$	Ir	Au	2.625	92.3	$[PtHg(mec)_2(MeNH_2)_2]^{2+}$	Pt	Hg	2.785	89.6
$[IrAu(dppm)_2(MeNC)_2]^{2+}$	Ir	Au	2.944	92.0	$[Pt(HgClBr)(^{i}PrNCHNTol)(damb)]$	Pt	Hg	2.833	92.8
$[IrAu(dppm)_2(MeNC)_2]^{2+}$	Ir	Au	3.059	91.7	$[Pt(HgCl\{NO_3\})(mec)_2(MeNH_2)_2]$	Pt	Hg	2.835	90.5
$[IrTl(crown)(CO)Cl]^{+}$	Ir	Tl	2.875	93.3	$[PtTl(crown)(CN)_2]^{+}$	Pt	Tl	2.911	93.6
$[PtCa(oxaz)_4Cl]^{-}$	Pt	Ca	2.960	92.4	$[PtTl(crown)(CN)_2]^{+}$	Pt	Tl	2.958	92.9
$[PtCu(meu)_2(NH_3)_2(H_2O)_2]^{2+}$	Pt	Cu	2.765	91.2	$[Au_2(Ph_2P\{CH_2\}_2)_2Cl_2]$	Au	Au	3.184	90.7
$[PtZn(meu)_2(NH_3)_2(H_2O)_3]^{2+}$	Pt	Zn	2.760	91.3	$[Au_6(terpy)_2Cl_{12}]$	Au	Au	3.300	90.8
$A\{ML_4\}_2$									
$[Rh_2Ag(btt)_2(cod)_2(ClO_4)]$	Rh	Ag	2.795	89.6	$[Pt_2Pd(meu)_4(NH_3)_4]^{2+}$	Pt	Pd	2.836	90.2
$[Rh_2Ag(dpma)_2Cl_3(CO)_2]$	Rh	Ag	3.352	91.7	$[Pt_2Pd(meu)_4(NH_3)_4]^{2+}$	Pt	Pd	2.839	89.9
$[Rh_2Ag(dpma)_2Cl_3(CO)_2]$	Rh	Ag	3.398	91.4	$[Pt_2Ag(acac)_2(C_6F_5)_4]$	Pt	Ag	2.674	90.4
$[Rh_2Au(nda)(PPh_3)_3(CO)_2]$	Rh	Au	2.690	91.3	$[Pt_4Ag_2(C_6Cl_5)_8Cl_4]^{2-}$	Pt	Ag	2.747	90.4
$[Rh_2Au(nda)(PPh_3)_3(CO)_2]$	Rh	Au	2.797	91.2	$[Pt_4Ag_2(C_6Cl_5)_8Cl_4]^{2-}$	Pt	Ag	2.755	90.3
$[Rh_2Hg(pz)_2(PPh_3)_2(CO)_2Cl_2]$	Rh	Hg	2.804	91.7	$[Pt_4Ag_2(C_6Cl_5)_8Cl_4]^{2-}$	Pt	Ag	2.765	90.4
$[Ir_2Ag(dpma)_2Cl_3(CO)_2]$	Ir	Ag	3.355	91.1	$[Pt_4Ag_2(C_6Cl_5)_8Cl_4]^{2-}$	Pt	Ag	2.782	89.3
$[Ir_2Ag(dpma)_2Cl_3(CO)_2]$	Ir	Ag	3.363	92.1	$[Pt_2Ag(C_6F_5)_4Cl_2(OEt_2)]^{-}$	Pt	Ag	2.759	89.5
$[Ir_2Sn(dpma)_2Cl_3(CO)_2]^{+}$	Ir	Sn	2.741	96.1	$[Pt_2Ag(C_6F_5)_4Cl_2(OEt_2)]^{-}$	Pt	Ag	2.782	89.8
$[Ir_2Sn(dpma)_2Cl_3(CO)_2]^{+}$	Ir	Sn	2.742	96.4	$[Pt_2Ag(C_6F_5)_6(OEt_2)]^{-}$	Pt	Ag	2.804	92.9
$[Ir_2Sn(dppb)_2Cl_4(CO)_2]$	Ir	Sn	2.752	98.2	$[Pt_2Ag(C_6F_5)_6(OEt_2)]^{-}$	Pt	Ag	2.815	94.0
$[Ir_2Sb(dpma)_2(CO)_2Cl_2F_2]^{+}$	Ir	Sb	2.655	95.5	$[Pt_3Ag(OH)_3(en)_3(NO_3)_3]^{+}$	Pt	Ag	2.839	92.6
$[Ir_2Au(SO_2)(dpma)_2(CO)_2Cl_2]^{+}$	Ir	Au	2.953	90.7	$[Pt_3Ag(OH)_3(en)_3(NO_3)_3]^{+}$	Pt	Ag	2.893	91.6
$[Ir_2Au(dpma)_2(CO)_2Cl_2]^{+}$	Ir	Au	3.012	91.2	$[Pt_3Ag(OH)_3(en)_3(NO_3)_3]^{+}$	Pt	Ag	2.899	92.5
$[Ir_2Tl(NO_3)(dpma)_2(CO)_2Cl_2]$	Ir	Tl	2.960	94.4	$[Pt_2Ag(met)_4(NH_3)_4]^{+}$	Pt	Ag	2.849	90.6
$[Ir_2Tl(NO_3)(dpma)_2(CO)_2Cl_2]$	Ir	Tl	2.978	94.2	$[Pt_2Ag(met)_4(NH_3)_4]^{+}$	Pt	Ag	2.884	90.2
$[Ir_2Pb(dpma)_2(CO)_2Cl_2I]^{+}$	Ir	Pb	2.831	95.8	$[Pt_2Ag(dppm)_2(CN)_2(CF_3SO_3)]$	Pt	Ag	3.002	90.5
$[Ir_2Pb(dpma)_2(CO)_2Cl_2I]^{+}$	Ir	Pb	2.854	95.5	$[Pt_4(HgCl)_2(C_6F_5)_8(OH)_2]^{2-}$	Pt	Hg	2.648	92.0
$[Pt_2D_9]^{5-}$	Pt	D	1.852	96.8	$[Pt_4(HgCl)_2(C_6F_5)_8(OH)_2]^{2-}$	Pt	Hg	2.678	93.5
$[Pt_2Mn(met)_4(NH_3)_4]^{2+}$	Pt	Mn	2.704	90.5	$[Pt_4(HgCl)_2(C_6F_5)_8(OH)_2]^{2-}$	Pt	Hg	2.714	91.9
$[Pt_2Cu(Hmec)_2(meu)_2(NH_3)_4]^{4+}$	Pt	Cu	2.681	90.4	$[Pt_4(HgCl)_2(C_6F_5)_8(OH)_2]^{2-}$	Pt	Hg	2.720	90.5
$[Pt_2Cu(meu)_4(NH_3)_4]^{2+}$	Pt	Cu	2.685	89.3	$[Pt_2Hg(C_6F_5)_7(OH)]^{2-}$	Pt	Hg	2.718	92.6
$[Pt_2Pd(meu)_4(NH_3)_4]^{3+}$	Pt	Pd	2.633	90.1	$[Pt_2(C_6F_5)_8Tl]^{2-}$	Pt	Tl	2.703	94.2
$[Pt_2Pd(meu)_4(NH_3)_4]^{3+}$	Pt	Pd	2.641	90.2	$[Pt_2Tl(met)_4(NH_3)_4]^{+}$	Pt	Tl	3.085	90.8
$[Pt_2Pd(met)_4(en)_2]^{3+}$	Pt	Pd	2.646	90.4	$[Pt_2(C_6F_5)_8Pb]$	Pt	Pb	2.782	93.9
A_2ML_4									
$[PtK_2I_4]$	Pt	K	3.437	90.0	$[PtTl_2(CN)_4]$	Pt	Tl	3.140	90.0
$[PtK_2(meu)_2I_2]$	Pt	K	3.688	90.0	Tl_2PdSe_2	Pd	Tl	2.923	90.0
$[PtAg_2(meu)_2(NH_3)_2(H_2O)(NO_3)]$	Pt	Ag	2.863	90.8	$[Au_3(dppe)_4]^{+}$	Au	Au	3.049	90.0
$[PtAg_2(meu)_2(NH_3)_2(H_2O)(NO_3)]$	Pt	Ag	2.896	89.1	$[Au_3(dppe)_4]^{+}$	Au	Au	3.052	89.9
$[Pt_3Ag_2(S_2CNEt_2)_6]^{2+}$	Pt	Ag	2.932	90.0	$[Au(Hdmg)_2][AuCl_2]$	Au	Au	3.260	90.0

[a] See Supporting Information for references.

toward the Rh−A interatomic region, whereas the antibonding combination (essentially p_z) is hybridized away from that bond (Figure 1). As a result, the AML_4 molecule is a better acceptor through its hybridized p_z orbital than the parent ML_4 complex through its unhybridized p_z orbital. Experimental evidence of the enhanced acceptor character of the metal atom in the AML_4 adduct relative to ML_4 will be invoked in the discussion below.

It is obvious that binding of two Lewis acids to the axial coordination positions is also possible, giving A_2ML_4 compounds. However, the resulting M−A bonds should be weaker than in AML_4 since only two electrons are available for two M−A bonds. Hence, this type of compound is more likely to occur for the more ionic M−A bonds ($A = K^+$, Tl^+; Table 1).

d^8-ML_4 Complexes as Acceptors. In principle, a d^8-ML_4 complex can behave as an acceptor by using its empty p_z orbital. In fact, many pentacoordinate complexes of d^8 metal ions have been isolated and characterized[5−8] (Table 2), the formation of a pentacoordinate species through the association of a fifth ligand being usually the key step in the ligand substitution processes.[9−13] Even if the pentacoordinate complexes may

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Table 2. Structural Data for Adducts of d^8-ML_4 Complexes with Lewis Bases (ML_4B)[a]

compound	M	B	M−B (Å)	α_B (deg)
$[\mathrm{Co(CO)(\{PPh_2\}_2NCMe_3)_2}]^+$	Co	C	1.796	102.5
$[\mathrm{Co_2(hmtaa)_2(CO_2H)}]^{3-}$	Co	C	2.061	93.8
$[\mathrm{Co_2(hmtaa)_2(CO_2H)}]^{3-}$	Co	O	2.278	92.5
$[\mathrm{Co(dmgBF_2)_2(py)}]^-$	Co	N	2.018	98.3
$[\mathrm{Co(ttp)(CO)(P\{OMe\}_3)}]^+$	Co	P	2.196	101.4
$[\mathrm{Ni(CN)_5}]^{3-}$	Ni	C	2.170	100.2
$[\mathrm{Ni(CN)_2(Me\text{-}phos)_3}]$	Ni	P	2.321	104.6
$[\mathrm{Ni(PMe_3)(\{HSC_6H_4S\}_2C_3H_6)}]^{2+}$	Ni	S	2.613	95.5
$[\mathrm{NiI(depe)_2}]^+$	Ni	I	2.797	96.3
$[\mathrm{Ru(dmpe)_2(PMe_3)}]$	Ru	P	2.297	103.6
$[\mathrm{Rh(SO_4)(NO)(PPh_3)_2}]$	Rh	P	2.410	95.8
$[\mathrm{RhCl(ttp)(SO_2)}]$	Rh	S	2.325	96.4
$[\mathrm{Rh(CO)(ttp)(SO_2)}]^+$	Rh	S	2.433	92.1
$[\mathrm{RhCl(PPh_3)_2(SO_2)}]_2$	Rh	S	2.370	97.6
$[\mathrm{RhCl(CO)(PPh_3)_2(SO_2)}]$	Rh	S	2.450	95.3
$[\mathrm{Rh_2Cl_2(NO)_2(dppm)_2}]^{2+}$	Rh	Cl	2.454	97.3
$[\mathrm{Pd(\{2\text{-}pyCH_2\}_3[9]aneN_3)}]^{2+}$	Pd	N	2.580	91.3
$[\mathrm{Pd(Me_2phen)(PhPMe_2)_3}]^{2+}$	Pd	N	2.588	92.8
$[\mathrm{Pd_2(quipy)_2}]^{4+}$	Pd	N	2.600	93.5
$[\mathrm{Pd_2(quipy)_2}]^{4+}$	Pd	N	2.633	95.1
$[\mathrm{PdCl(phen)(PPh_3)_2}]^+$	Pd	N	2.680	93.4
$[\mathrm{Pd(\{CF_3CO\}CH)_2(P\{o\text{-}MeC_6H_4\}_3)}]$	Pd	O	2.795	93.1
$[\mathrm{PdCl(\{OH\}_4Me_8[14]aneP_4)}]^+$	Pd	Cl	2.831	96.5
$[\mathrm{PdCl_2(PhPMe_2)_3}]$	Pd	Cl	2.956	94.2
$[\mathrm{PdCl(dbtp)}]^+$	Pd	Cl	3.106	87.6
$[\mathrm{PdCl(tpas)}]^+$	Pd	As	2.860	90.7
$[\mathrm{PdBr_2(2\text{-}Ph\text{-}isophosphindoline)_3}]$	Pd	Br	2.923	95.3
$[\mathrm{PdBr_2(2\text{-}Ph\text{-}isophosphindoline)_3}]$	Pd	Br	3.017	94.5
$[\mathrm{PdBr_2(Et\text{-}phos)_3}]$	Pd	Br	2.936	96.3
$[\mathrm{Ir(CO)(PPh_3)_2(\{\{MeO\}_2P\}_2NMe)}]^+$	Ir	C	1.901	105.7
$[\mathrm{Ir(\{CN\}_4im_2)(cod)(PPh_3)}]^-$	Ir	N	2.322	97.9
$[\mathrm{Ir(MeNC)(dppe)_2}]^+$	Ir	P	2.345	102.4
$[\mathrm{Ir(CO)(dppe)_2}]^+$	Ir	P	2.370	99.3
$[\mathrm{IrCl(CO)(dpma)(SO_2)}]_2$	Ir	S	2.413	95.0
$[\mathrm{IrCl(CO)(PPh_3)_2(SO_2)}]$	Ir	S	2.488	94.4
$[\mathrm{Ir(SnCl_3)_2(CO)(dpma)}]^-$	Ir	Sn	2.591	103.8
$[\mathrm{Pt(CN)(phen)_2}]^+$	Pt	N	2.761	92.5
$[\mathrm{Pt(\{CF_3CO\}CH)_2(PCy_3)}]$	Pt	O	2.772	91.3
$[\mathrm{PtCl_2(cyclotrithiatriveratrilene)}]$	Pt	S	2.860	91.7
$[\mathrm{Pt([9]aneS_3)_2}]^{2+}$	Pt	S	2.878	90.8
$[\mathrm{Pt([9]aneS_3)_2}]^{2+}$	Pt	S	2.923	90.4
$[\mathrm{Pt(GeCl_3)_5}]^{3-}$	Pt	Ge	2.481	100.7
$[\mathrm{PtBr_2(Me\text{-}phos)_3}]$	Pt	Br	3.027	94.4
$[\mathrm{PtBr_2(Et\text{-}phos)_3}]$	Pt	Br	3.141	94.0
$[\mathrm{AuCl_3(Me_2phen)}]$	Au	N	2.584	91.8
$[\mathrm{AuBr(CN)_2(phen)}]$	Au	N	2.608	91.3
$[\mathrm{AuBr_3(Me_2phen)}]$	Au	N	2.615	92.6
$[\mathrm{Au(dmp)(phen)(PPh_3)}]^{2+}$	Au	N	2.627	92.6
$[\mathrm{AuBr_3(pq)}]$	Au	N	2.636	91.6
$[\mathrm{AuCl_3(pq)}]$	Au	N	2.672	90.8
$[\mathrm{AuCl(tpp)}]$	Au	Cl	3.010	90.4
$[\mathrm{\{AuCl_2(bipy)\}_2Cl}]^+$	Au	Cl	3.211	91.2
$[\mathrm{\{AuCl_2(bipy)\}_2Cl}]^+$	Au	Cl	3.224	90.7

[a] See Supporting Information for references.

present a trigonal bipyramidal structure, we will assume a square pyramidal structure except when otherwise specified, since the two structures are close in energy and their interconversion has low-energy barriers.[5,14]

A simplified diagram for the orbital interaction between ML_4 and a Lewis base B is shown in Figure 2. In this case, the d_{z^2} orbital, acquires M−B antibonding character, attenuated by its hybridization with p_z. This molecular orbital has higher energy than d_{z^2} in ML_4 and is hybridized away from the M−B bond. In other words, the BML_4 group is a better electron donor than its parent ML_4 complex.

But things are not always simple. In our EH calculations, the interaction of $[RhCl_4]^{2-}$ with an additional base is stabilizing for B = CO but appears to be destabilizing for B = Cl^-. In fact, the σ contribution represented in Figure 2 is stabilizing for both ligands. In addition, there is a π-type interaction of the occupied d_{xz} and d_{yz} metal orbitals with the empty π^* orbitals of CO which provides additional stability, but with the occupied p_x and p_y orbitals of Cl^- (thus destabilizing the M−Cl bond). Since the EH calculations cannot be relied on in their quantitative aspects, they may not adequately account for the relative weight of the stabilizing and destabilizing contributions. Therefore, such results should be interpreted as indicative of a poorer stability of the BML_4 adduct when B is a π-basic ligand than when it is a π-acid one.

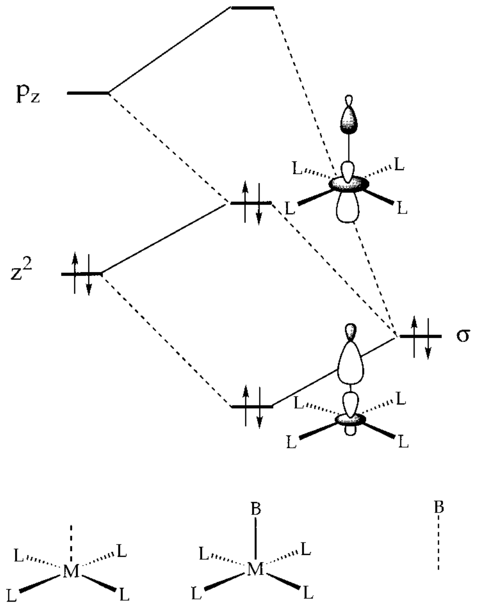
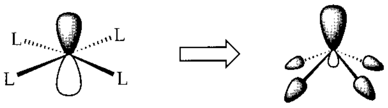
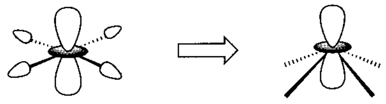


Figure 2. Schematic diagram for the σ-type orbital interaction between a square planar d^8-ML_4 complex and a Lewis base B along the axial direction.

Pyramidality of the AML_4 and BML_4 Complexes. It is interesting to note that the planarity of the ML_4 fragment is lost to different degrees in the AML_4 and the BML_4 derivatives, a fact for which a simple explanation can be found. We have previously shown[15] that the p_z orbital of the square planar complexes becomes strongly hybridized away from the ligands upon pyramidalization. In this way, it is made as little M−L antibonding as possible (**2a**). In contrast, d_{z^2} is M−L antibonding in the planar ML_4 fragment and becomes less antibonding upon pyramidalization; hence, no significant hybridization of this orbital results (**2b**).



2a



2b

The outcome of the different behavior of p_z and d_{z^2} upon pyramidalization of the ML_4 fragment is that the acceptor ability of ML_4 (**1a**) improves upon pyramidalization, whereas its donor properties (**1b**) are practically insensitive to such structural changes. As a consequence, an important degree of pyramidalization is to be expected when the metal atom acts as an

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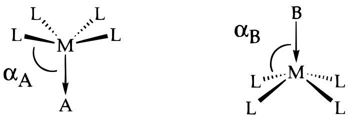
Table 3. Calculated Overlap Populations for the Rh−B Bond in [Rh^ICl_4B] and Its Adducts [ARh^ICl_4B] and for the Rh−A Bond in [ARh^ICl_4] and Its Adducts [ARh^ICl_4B]

B	[Rh^ICl_4B]	[$(ClAu)Rh^ICl_4B$]	[$HRhCl_4B$]
Cl^-	0.193	0.294	0.283
CO	0.736	0.751	0.772
A	**[ARh^ICl_4]**	**[$ARh^ICl_4Cl_{ax}$]**	**[$ARh^ICl_4(CO)$]**
AuCl	0.175	0.286	0.400
H^+	0.501	0.528	0.539

acceptor through its p_z orbital, but little or no pyramidalization should occur when it behaves as a donor through its d_{z^2} orbital. We note here also that a π-acid ligand in the axial position induces a larger pyramidalization than a π-basic one.

The pyramidality of the metal atom relative to A in the AML_4 compounds, α_A (see **3**), is predicted from EH calculations at 93.0° (A = H^+), 90.3° (A = AuCl), and 89.7° (A = Na^+), whereas, for the BML_4 complexes, the pyramidality angle α_B is predicted at 98.3° (B = Cl^-) and 104.9° (B = CO), using $[RhCl_4]^{3-}$ as a model for ML_4. These results are in excellent agreement with the qualitative reasoning just discussed. Evidence for the different pyramidality effect of Lewis bases and acids can be found in Tables 1 and 2 and will be discussed below.



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AML_4B Derivatives. If a ML_4 complex can separately bond to an acid or to a base, it can also bond to an acid and a base simultaneously, thus giving place to hexacoordinate AML_4B species, which could in principle be obtained through reactions 1 or 2. A particular pathway for the formation of such complexes is that of the oxidative addition of an AB molecule (e.g., CH_3X) to ML_4 (reaction 3), although formal oxidation of the metal atom is not necessary for the formation of the AML_4B compounds.

$$A + ML_4 \rightarrow AML_4 \tag{1a}$$

$$AML_4 + B \rightarrow AML_4B \tag{1b}$$

$$B + ML_4 \rightarrow ML_4B \tag{2a}$$

$$ML_4B + A \rightarrow AML_4B \tag{2b}$$

$$AB + ML_4 \rightarrow AML_4B \tag{3}$$

As seen above, an AML_4 adduct forms a stronger bond to a Lewis base and a BML_4 derivative forms a stronger bond to a Lewis acid than the parent square planar complex. Hence, AML_4B complexes are expected to be especially stable. In other words, the presence of an acceptor A, strengthens the bond in *trans* to a donor B and *vice versa*. The computational results supporting this reasoning, presented in Table 3, are self-explanatory.

Even if one can think of the AML_4B derivatives as octahedral complexes, given the different effects of A and B on the pyramidalization of the metal atom, the average LMB bond angle (α_B) is expected to be greater than 90° and larger than the average LMA bond angle (α_A). Angle optimization for the $[(B)RhCl_4(AuCl)]^{3-}$ model complexes confirms this (e.g., α_B = 100°, α_A = 80° for B = CO; α_B = 96°, α_A = 84° for B = Cl^-).

Discussion

The theoretical model presented above is useful not only for providing a general understanding of the bonding and structure of the adducts of square planar complexes but also in allowing the systematization of a wealth of experimental data, in particular through structural correlations. In this section we discuss first the chemical reactivity of the ML_4 compounds and of its AML_4 and BML_4 derivatives and then the structural data for the AML_4, BML_4, and AML_4B complexes in light of the theoretical results discussed above.

Chemical Reactivity. The dual base−acid properties of the metal atom in a square planar complex, and the effect of axial groups thereof, have a bearing on its reactivity as nucleophile/electrophile. According to the theoretical discussion above, one might expect square planar complexes to act as nucleophiles through the z^2 electron pair, and the addition of an apical ligand should enhance its nucleophilicity. The nucleophilic character of square planar complexes in a number of reactions has been proposed by several authors for compounds of Os(0),[16] Rh(I),[17,18] Co(I),[19−21] and Pt(II).[22] Furthermore, the nucleophilicity of reduced cobaloximes has been found to depend on the nature of the axial ligand,[19] and the addition of a fifth ligand (iodide,[23−27] amines,[24] or acetate[25]) to square planar complexes has been reported to enhance their nucleophilicity.

On the other hand, our theoretical results suggest that the electrophilic properties of a d^8 metal should be enhanced through coordination of a Lewis acid. Consistently, it has been found that the binding of a primary ammonium ion to $[RhCl_2(CO)_2]^-$ diminishes its nucleophilicity.[26] On the other hand, the fact that the addition of LiI to $[RhCl_2(CO)_2]^-$ results in a stronger nucleophilic character of the complex is explained by the competition between the iodide and the Li^+ ions,[26] with the former being the prevailing effect.[25]

Oxidative addition reactions of the ML_4 complexes result in the coordination of both a donor and an acceptor (eq 3, where AB can be a hydrogen halide or an alkyl halide[28,29]). In many instances, such reactions have been claimed to proceed through an associative S_N2 mechanism.[17,18,30−32] If the first step of such

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Table 4. Structural Data for Adducts of d^8-ML_4 Complexes with an Acid and a Base (*AML_4B*)[a]

compound	M	A	B	M−A (Å)	α_A (deg)	M−B (Å)	α_B (deg)	AMB (deg)
$[RuPd\{(Ph_2P)py\}_2(CO)_2Cl_2]$	Ru	Pd	Cl	2.660	87.4	2.477	92.6	175.3
$[\{RuMe(PMe_3)_4\}_2Hg]$	Ru	Hg	P	2.798	85.9	2.325	93.9	161.2
$[\{RuMe(PMe_3)_4\}_2Hg]$	Ru	Hg	P	2.800	86.0	2.313	93.7	158.2
$[Rh_2(dmmm)_2(CO)(I)]^+$	Rh	Rh	I	2.735	85.4	2.848	94.6	177.1
$[Rh_2(dmmm)_2(CO)_2]^{2+}$	Rh	Rh	C	2.777	82.6	1.945	97.0	176.3
$[RhPd\{(Ph_2P)py\}_2Cl_3(CO)]$	Rh	Pd	Cl	2.594	88.4	2.499	91.7	174.7
$[Rh_2Pd(dpma)_2Cl_3(CO)_2]^+$	Rh	Pd	Cl	2.698	88.6	2.448	91.6	175.0
$[Rh_2Sn_2\{(Ph_2P)_2py\}_2(CO)_2Cl_6]$	Rh	Sn	Cl	2.602	89.0	2.489	91.3	172.1
$[RhPt(dppm)_2(MeNC)_3Cl]^{2+}$	Rh	Pt	Cl	2.688	90.0	2.516	90.0	173.1
$[RhPt(dapm)_2Cl_3(CO)]$	Rh	Pt	Cl	2.692	88.3	2.511	91.7	175.5
$[RhPt(dppm)_2(MeNC)_3I]^{2+}$	Rh	Pt	I	2.703	89.5	2.807	90.5	175.0
$[RhPt(dppm)_2(MeNC)_4]^{3+}$	Rh	Pt	C	2.708	88.8	2.060	91.0	178.4
$[RhPt(dapm)_2I_3(CO)]$	Rh	Pt	I	2.737	86.0	2.731	94.2	174.4
$[Rh_2Hg(pz)_2(PPh_3)_2(CO)_2Cl_2]$	Rh	Hg	Cl	2.586	89.5	2.474	90.7	172.4
$[Os(AgO_2CCF_3)(CO)_3(PPh_3)_2]$	Os	Ag	C	2.712	79.9	1.904	100.1	172.6
$[Ir_2Ag(dimen)_4(PPh_3)_2]^{3+}$	Ir	Ag	P	2.640	84.5	2.385	95.6	173.9
$[Ir_2Ag(dimen)_4(Me_2SO)_2]^{3+}$	Ir	Ag	S	2.642	84.6	2.458	95.4	170.4
$[Ir_2Au(dpma)_2(CO)_2Cl_4]^+$	Ir	Au	Cl	2.806	89.4	2.476	90.5	176.3
$[Ir_2Au(dpma)_2(CO)_2Cl_4]^+$	Ir	Au	Cl	2.812	89.6	2.458	90.3	179.6
$[IrAu(dppm)_2(MeNC)_3]^{2+}$	Ir	Au	C	2.817	81.9	2.090	98.1	177.6
$[Ir_2Au(SO_2)(dpma)_2(CO)_2Cl_2]^+$	Ir	Au	S	3.133	87.9	2.525	91.8	163.7
$[Ir_2(dimen)_4(PPh_3)Au(PPh_3)]^{3+}$	Ir	Au	Ir	2.607	85.4	2.986	94.7	172.9
$[IrHg(CO)(PPh_3)_2Cl_3]_2$	Ir	Hg	Cl	2.570	88.8	2.452	91.3	177.1
$[IrHg(CO)(PPh_3)_2Br_2Cl]_2$	Ir	Hg	Br	2.578	88.4	2.586	90.0	176.6
$[IrHg_2Cl_5(CO)(dppm)_2(AuCl)]_2$	Ir	Hg	P	2.618	90.8	2.385	88.9	168.7
$[IrHg(TolN_3Et)_2(cod)_2Cl]_2$	Ir	Hg	N	2.618	92.1	2.195	89.1	143.5
$[IrTl(MeCO_2)_4(CO)(PPh_3)_2]$	Ir	Tl	O	2.611	91.7	2.081	88.3	174.9
$[PtHg(Me_2NCH_2C_6H_4)_2(MeCO_2)_2]$	Pt	Hg	N	2.513	89.8	2.317	90.7	166.7

[a] See Supporting Information for references.

reaction is the nucleophilic attack of the metal atom to an alkyl halide,[17,18,22,32] it should be favored by the previous coordination of a Lewis base, as discussed above. A rate-enhancing effect of an added Lewis base on the oxidative addition reaction of alkyl halide over square planar complexes of Rh(I)[23−26] and Ir(I)[27] has in fact been detected experimentally. Even if pentacoordinate intermediate species have not been detected in most cases, these have been postulated as reaction intermediates because kinetic experiments have shown that pentacoordinate complexes are better nucleophiles than tetracoordinate ones.[26,27] A related piece of information comes from the reactions between methyl iodide and $[IrCl(CO)(Me_2PR)_2]$, whose rates of reaction depend on the substituents on the phosphine ligands, being faster for R = *o*-$MeOC_6H_4$, due to an electron donation from the methoxy group to the Ir atom.[33] One of the reviewers has called our attention to a related theoretical study of the oxidative addition of atomic Pd to CH_3Cl. In it, the predominant oxidative insertion mechanism is shown to be changed to a nucleophilic substitution upon coordination of a chloride anion to the Pd atom.[34]

If the rate-determining step of an oxidative addition reaction is an electrophilic attack,[35] the presence of a Lewis acid which can eventually bind to the square planar complex is expected to lower the activation energy and accelerate the rate of the oxidative addition reaction. In fact, in the reaction of $[Ir(cod)L_2]^+$ with HCl the protonation of the metal atom has been found to be the rate-determining step, with the coordination of the chloride ion being a subsequent fast step. By using acids with a non coordinating anion (e.g., HBF_4), the HML_4 adduct can even be isolated.[36]

Structural Trends for the AML_4 Complexes. Some relevant structural data of square pyramidal AML_4 and the related $A\{ML_4\}_2$ complexes are presented in Table 1. Notice the variety of Lewis acids than can bind to a d^8 metal center. In addition, the existence of intramolecular M···H interactions, explained by the donor ability of the d_{z^2} orbital,[37] has been detected in a number of square planar complexes of Rh(I),[38,39] Pt(II),[40−45] Pd(II),[46,47] or even Ni(II).[48] However, no hydrides are found in that list, and we will come back to discuss this aspect below.

As for the pyramidalization of the metal, the distribution of the AML bond angles (α_A) is presented as a histogram in Figure 3 (top). There, it is seen that all of the experimental values fall in the range 88° < α_A < 98°, with the largest number of compounds clustered around 90−92°, as expected from the qualitative orbital discussion above. The fact that no correlation

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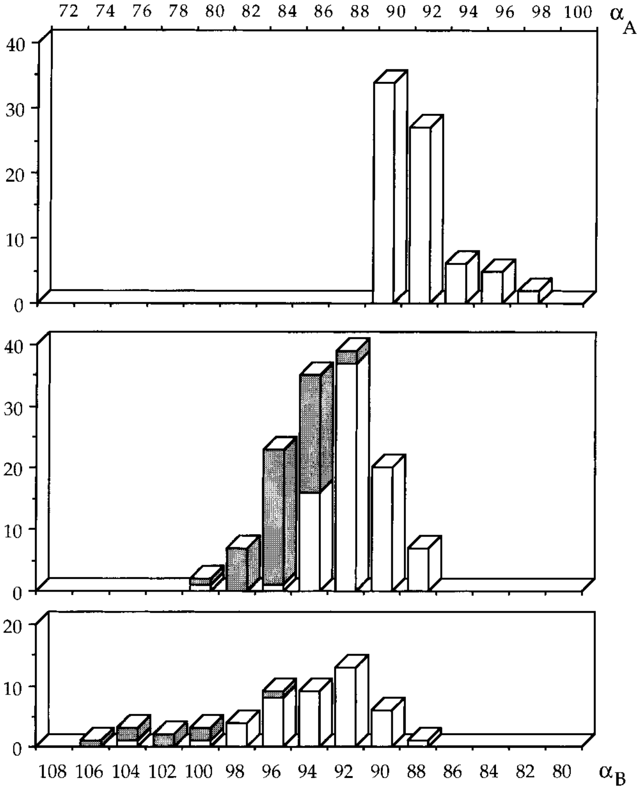

Figure 3. Distribution of the experimental pyramidality angles (see **3**) in the adducts of d^8-ML$_4$ complexes of types AML$_4$ (top), AML$_4$B (center), and ML$_4$B (bottom), where A and B are a Lewis acid and base, respectively. The shaded areas indicate the compounds in which B is a strong σ-donor.

is found between the angle α_A and the M−A bond distance[49] can be attributed to the small range of experimental angles and the wide variety of compounds.

Structural Trends for the BML$_4$ Complexes. The situation is clearly different for the BML$_4$ complexes. As expected, a marked deviation from planarity of the ML$_4$ group is observed upon coordination of B (Table 2 and Figure 3, center), with the BML angles in the range $87° < \alpha_B < 106°$. It is noteworthy that those groups B considered as *strong σ*-donors (phosphines, carbonyl, isocyanides) present larger values of α_B than poorer donors (alkoxides, amines, etc.), in excellent agreement with the differences found in our calculations with CO ($\alpha_B = 104.9°$) and Cl$^-$ ($\alpha_B = 98.3°$) axial groups.

With the wide range of pyramidality angles presented by the BML$_4$ complexes, one should expect to observe a dependence of the B−M bond distances on the angle α_B.[15,49−51] However, there are no large families of similar compounds to make such a study feasible. Small groups of compounds apparently following the expected trend (shorter B−M distance for the larger angle α_B) are those with the following M−B bonds: Rh−S (with ttp or with PPh$_3$), Pd−Cl, Pd−Br (with the 2-phenylisophosphindoline ligand), Ir−P, Ir−S, Pt−S, and Pt−Br. It must also be noted that, at first sight, the compounds with Au−N and Pd−N bonds do not follow the expected trend. Although a more general analysis of the structural data is difficult due to the diversity of complexes and Lewis bases structurally characterized (Table 2), we attempt such an analysis

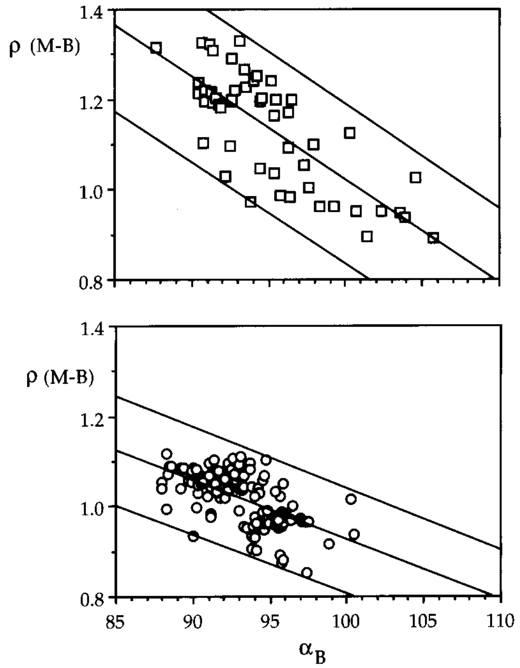

Figure 4. Scattergram of the relative bond lengths ρ_{M-B} (see eq 4) as a function of the pyramidality α_B for the adducts of square planar complexes of the type ML$_4$B (top, squares) and AML$_4$B (bottom, circles).

by using a relative bond length ρ_{M-B} which defines the ratio of the experimental bond distance (d_{M-B}) to the sum of the covalent radii (r_M and r_B, respectively):

$$\rho_{M-B} = \frac{d_{M-B}}{r_M + r_B} \tag{4}$$

The resulting values are plotted against α_B in Figure 4 (squares). No good correlation can be found between the two structural parameters, which is not surprising given the rough approximation used to represent bond distances of different atomic pairs with a single parameter and the diversity of compounds under consideration. Nevertheless, the general trend is that the distribution of the experimental distances is centered at smaller values for the larger pyramidality angles. Such tendency will be discussed in more detail below, in conjunction with the data for the AML$_4$B compounds.

Structural Trends for the AML$_4$B Complexes. As seen in the previous sections, the attachment of an acid to the ML$_4$ molecule enhances the acidity (Figure 1), whereas the coordination of a fifth Lewis base enhances the basicity of the metal atom (Figure 2). One should therefore expect that the M−A and M−B bonds in the AML$_4$B complexes reinforce each other, being stronger than in the AML$_4$ and BML$_4$ compounds, respectively. Such effect can be detected in the structural data for M−B bonds (Tables 2 and 4). It can be better seen in Figure 4, where for the same pyramidality angle α_B the M−B distances are in general shorter (i.e., ρ_{MB} smaller) in the AML$_4$B family than in the ML$_4$B compounds. One can also observe in Figure 4 that the α_B angles are larger in the ML$_4$B complexes than in the AML$_4$B family.

Perhaps the best illustration of the M−A bond-strengthening ability of the basic groups in *trans* is provided by a binuclear complex of Rh[52] (**4**), in which the metal atom with an additional chloride ligand is strongly bonded to an Hg^{2+} ion (2.59 Å),

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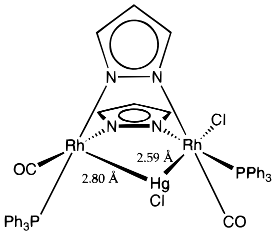

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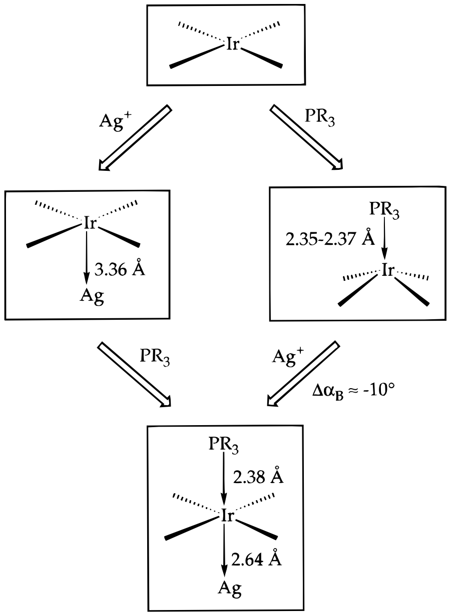
whereas the metal atom without a *trans*-ligand forms a weaker bond (2.80 Å) to the same ion. The synergetic strengthening of the M−A and M−B bonds in the AML_4B compounds can also be appreciated in the trio of related compounds represented in **5**: the Ir→Ag distances of 3.36 Å[2] in compounds of type AML_4 (Table 1) are shortened to 2.64 Å upon addition of a Lewis base such as a phosphine[53] or DMSO.[54] Conversely, the P−Ir distances in the $[(PR_3)IrL_4]$ compounds[55,56] are practically identical when a Lewis acid is present in *trans*. However, it must be noticed that the pyramidality angle (α_B) for the Ir−P bond is much smaller in the presence of the Lewis acid. This means that the weakening of the Ir−P bond due to the smaller pyramidality angle and the strengthening due to the effect of the *trans* acid are practically compensated. Such compensation of effects can also be appreciated in the Ru−P[57,58] and Rh−Cl[52,59−66] bonds. When the pyramidality angle α_B changes little from BML_4 to AML_4B, as for the Pt−N bonds (92.5[67] and 90.7°,[68] respectively), the distance is clearly shorter in the compound with the acid group in *trans* (2.317 *vs* 2.761 Å).



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It is also remarkable that whenever a proton occupies one of the axial positions, one finds also another ligand in *trans*, due to the important enhancement of the Lewis acidity induced by the M−H bond, giving short M−B distances[69] and allowing the coordination of bases with low coordinating ability.[70,71]

The donor ability of the metal atom in a square planar d^8-ML_4 complex is clearly demonstrated by an interesting family of compounds in which such complex acts as a ligand through its metal atom toward a d^8-ML_3 fragment. A theoretical analysis of bonding in this particular class of compounds and a literature account has been recently published.[72] The qualitative bonding model presented here can be extended to explain the metal···metal interactions in dimers and chains of d^8-ML_4 complexes[73,74] and to explain how the addition of a Lewis acid to one of the metal atoms in d^8···d^8 dimers reinforces the M···M contact.

Conclusions

Our combined theoretical and structural correlation study of the axial bonding capabilities of the square planar d^8-ML_4 complexes allowed us to obtain quite general conclusions rooted on simple qualitative bonding ideas and provide a rationale for a large body of structural data.

Upon bonding of a Lewis acid at an axial coordination site, the resulting AML_4 adduct becomes a better axial acceptor than the parent ML_4 complex. $A_2\{ML_4\}$ compounds can also be formed, although the A−M bonds are weaker in this case than in AML_4. In a similar way, a BML_4 molecule is a better electron donor than its parent ML_4 complex. These adducts are expected to be more stable if B is a π-acid ligand. A synergetic effect can be observed, since the presence of an acceptor A bonded to ML_4 strengthens the bond in *trans* to a donor B, and *vice versa*.

The addition of axial groups modifies the reactivity of the metal center. In particular, the oxidative addition reactions on ML_4 complexes which occur through an associative S_N2 mechanism should be favored by the previous coordination of a Lewis base if the rate-determining step is the nucleophilic attack of the metal atom. Conversely, in those cases in which the rate-determining step is an electrophilic attack the presence of a Lewis acid is expected to speed up the oxidative addition reaction.

An important degree of pyramidalization at the metal atom is to be expected when the metal atom acts as an acceptor through its p_z orbital, but little or no pyramidalization should occur when it behaves as a donor through its d_{z^2} orbital. Hence, in AML_4 adducts the experimental pyramidalities fall in the

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range 88° $< \alpha_A <$ 98°. In contrast, in the BML_4 complexes angles in the range 87° $< \alpha_B <$ 106° are found, with *strong* σ-donors presenting larger values of α_B than poorer donors. An observed trend is that for the same pyramidality angle α_B the M−B distances are in general shorter in the AML_4B family than in the AML_4 one.

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Appendix

Computational Details. Extended Hückel calculations of molecular orbitals [75] were carried out using the modified Wolfsberg−Helmholz formula[76] and standard atomic parameters,[75,77−81] with the help of the CACAO program.[82] The models used for our molecular orbital calculations were the complex $[RhCl_4]^{3-}$ (D_{4h} symmetry) and its adducts $[ZRhCl_4]^{3-}$ (C_{4v} symmetry), with Z = H^+, AuCl, Na^+, Cl^- and CO, using the following: bond distances,[83] Rh−H = 1.57 Å,[84] Rh−Au = 2.70 Å, Rh−Na = 2.70 Å, Rh−Cl = 2.40 Å, Rh−C = 1.80 Å, Au−Cl = 2.28 Å, and C−O = 1.15 Å, and Rh−Au−Cl and Rh−C−O bond angles of 180°.

Database Search. The collection of structural data was obtained mostly through a systematic search of the Cambridge Structural Database[85] for compounds of general formulas ML_4 (square planar), AML_4, or BML_4 (square pyramidal), and AML_4B. M was imposed to be a metal at its oxidation state with a d^8 configuration: Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), Au(III), Ru(0), and Os(0). The donor atoms, L and B, were allowed to be any element of the periodic groups 14, 15, 16, or 17. As acceptor atoms A, all metals and semimetals were allowed in the search. The presence of H in the A position was admitted if it is the only hydrido ligand present in the complex.

Supporting Information Available: Tables listing references for the structural data in the tables and of abbreviations used for the ligands (15 pages). Ordering information is given on any current masthead page.

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