

Valence Shell Charge Concentrations at Pentacoordinate d^0 Transition-Metal Centers: Non-VSEPR Structures of Me_2NbCl_3 and Me_3NbCl_2

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Abstract: The molecular structures of the monomeric, pentacoordinated methylchloroniobium(IV) compounds Me_3NbCl_2 and Me_2NbCl_3 have been determined by gas electron diffraction (GED) and density functional theory (DFT) calculations, and, for Me_3NbCl_2 , by single crystal X-ray diffraction. Each of the molecules is found to have a heavy-atom skeleton in the form of a trigonal bipyramid (TBP) with Cl atoms in the axial positions, in accord with their vibrational spectra. The TBP is somewhat distorted in the case of Me_2NbCl_3 with the two axial Nb–Cl bonds bent *away* from the equatorial, slightly shorter Nb–Cl bond. In the case of Me_3NbCl_2 , moreover, the X-ray model suggests structural distortions

away from the idealized C_{3h} geometry, in line with the results of quantum chemical calculations. Structure optimizations by DFT calculations and least-squares refinement to the GED data yield the following structural parameters (calcd/exptl; eq = equatorial; ax = axial; distances in Å, angles in degrees; average values in $\langle \rangle$ brackets): Me_3NbCl_2 , in C_{3v} symmetry, Nb–Cl $\langle 2.370 \rangle / \langle 2.319(3) \rangle$, Nb–C 2.173/2.152(4), C–H $\langle 1.096 \rangle / 1.124(5)$, $\angle \text{NbCH}$ $\langle 109.3 \rangle / 105.2(8)$, $\angle \text{ClNbC}$ 92.2/93.3(2), $\angle \text{CNbC}$ 119.9/119.7(1); Me_2NbCl_3 , in C_{2v} symmetry, Nb–Cl_{ax}

2.361/2.304(5), Nb–Cl_{eq} 2.321/2.288(9), Nb–C 2.180/2.135(9), C–H $\langle 1.094 \rangle / 1.12(1)$, $\angle \text{Cl}_{ax}\text{NbCl}_{eq}$ 98.5/96.5(6), $\angle \text{CNbC}$ 121.0/114(2), $\angle \text{NbCH}$ $\langle 108.9 \rangle / 109(2)$. The electronic structures of Me_2NbCl_3 and Me_3NbCl_2 have been explored by rigorous analysis of both the wavefunction and the topology of the electron density, employing DFT calculations. Hence the structures of these compounds are shown to reflect repulsion between the Nb–C and Nb–Cl bonding electron density and charge concentrations induced by the methyl ligands in the valence shell of the Nb atom and arising mainly from use of Nb(4d) functions in the Nb–C bonds.

Keywords: charge density • gas electron diffraction • niobium

Introduction

Pentacoordinate molecules are intriguing as they possess no low-energy geometry with equivalent sites: the characteristic fluxionality of many such systems derives from the energetic proximity of, and facile interconversion between, the trigonal bipyramid (TBP) and the square-based pyramid (SQP). Typical examples are coordinatively unsaturated, allowing for facile inter- as well as intramolecular ligand exchange,^[1] and such systems are apt also to display the lasting effects of intermolecular interaction or exchange, as witnessed by the solid-state structure of PCl_5 .^[2] Pentacoordinate derivatives of the Group 15 elements played a central role four decades ago in the formulation and refinement of the VSEPR theory.^[3] The TBP-derived structures deduced by gas electron diffraction (GED) studies of molecules such as Me_2PF_3 ^[4] and Me_3PF_2 ^[5] led to the development of concepts such as apicophilicity, and to much discussion of the bonding displayed by such hypervalent main group systems.^[6] By

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contrast, analogous derivatives of the Group 5 elements V, Nb, and Ta have received relatively little attention. Thus, although the compounds $\text{Me}_n\text{NbCl}_{5-n}$ ($n=1-3$) have been known for three decades,^[7] no structural studies of these or other gaseous monomeric species of the type $\text{Me}_n\text{MX}_{5-n}$ ($M = \text{V, Nb, or Ta; X} = \text{halogen; } n = 1-5$) have been reported to date, with the exceptions of TaMe_5 ,^[8] Me_3TaF_2 ,^[9] and Me_3TaCl_2 .^[10]

Mononuclear pentavalent compounds of the Group 5 elements with monodentate ligands are generally found to resemble analogous derivatives of the Group 15 elements in adopting a TBP coordination geometry. There are, however, some exceptions, notably TaMe_5 ,^[8] SbPh_5 ,^[11] and BiPh_5 ,^[12] in each of which the five-coordinate central atom forms an SQP rather than a TBP. No single reason for this change is universally recognized. Although electronic effects are important, there is evidence, at least for selected main group compounds,^[13] that ligand–ligand interactions play a significant part in dictating the preference for a particular geometry.

The past decade has witnessed a realization that the coordination geometry of d^0 transition-metal (TM) centers is controlled by factors distinct from those espoused by VSEPR theory in its simplest form.^[14] Since the pioneering studies by Eisenstein et al.,^[15] who predicted a non-VSEPR geometry for $[\text{TiH}_6]^{2-}$ on the basis of extended Hückel calculations, several prominent examples of non-VSEPR d^0 TM structures—most notably $[\text{ZrMe}_6]^{2-}$,^[16] Me_2TiCl_2 ,^[17] and $\text{W}(\text{CH}_3)_6$ ^[18,19]—have been confirmed by structural and spectroscopic techniques, or have been predicted by theoretical studies.^[14,19] Several models based on MO theory have been advanced to rationalize this phenomenon,^[14,19] but these cannot compete with the simplicity and success rate of the VSEPR model in predicting the geometries of main group molecules. It is not surprising, therefore, that attempts have been made to develop further the VSEPR concept. In a pioneering study, Gillespie et al.^[20] proposed topological analysis of the charge density as a non-empirical way of accounting for the polarization of metal atoms, and discovered so-called ligand-induced charge concentrations (LICCs) to exist *trans* to the $M-X$ bonds in the non-linear alkaline-earth dihalides. As with these geometries, which are also successfully predicted by the polarized ion model,^[21] so too more generally does polarization of the metal by the coordinating ligands seem to be a primary factor in promoting distortion away from the expected VSEPR geometries. In fact, Bader et al. had shown earlier that the presence of ligands in covalent or polar molecules induces local charge concentrations (CCs) in the valence shell of the central atom which are revealed by an Atoms-in-Molecules (AIM) theory analysis as (3,-3) critical points (CPs) in the Laplacian function $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ of the charge density.^[22] Furthermore, the number and relative positions of these so-called valence shell charge concentrations (VSCCs) not only depend on, but also counteract, the number and relative positions of the localized electron pairs (electron pair domains) associated with the bonding and non-bonding electron pairs of the

VSEPR model. Despite the success of this concept in predicting the geometries of some non-VSEPR compounds, such as Me_2TiCl_2 ,^[23] the true nature and origin of the VSCCs remained unclear. In a recent experimental and theoretical charge density study of agostic d^0 TM alkyls, however, VSCCs have been shown to originate in the formation of covalent $M-C$ bonds employing valence d orbitals at the metal, thereby endowing the extended VSEPR concept with a rational physical basis.^[24]

In order to develop the extended VSEPR model further and to test its predictive power, we have searched for new non-VSEPR benchmark structures. In this respect, heteroleptic d^0 derivatives of Group 5 offer a unique opportunity on account of their highly flexible coordination geometry, which leads to a variety of structural possibilities. The relatively high volatility of the niobium compounds Me_2NbCl_3 and Me_3NbCl_2 , allied to their accessibility and ease of purification, has therefore prompted us to determine the structures of these molecules not only by quantum chemical calculations, but also experimentally by GED and single-crystal X-ray measurements. The results invite comparison with those of related pentacoordinate molecules centered on a Group 5 or Group 15 element, and also with the structures reported for other non-VSEPR compounds, such as the tetra-coordinate Group 4 molecule Me_2TiCl_2 ^[17] and the penta-coordinate Group 7 one Me_3ReO_2 .^[25]

Experimental and Computational Section

Me_2NbCl_3 and Me_3NbCl_2 were each prepared by the reaction of NbCl_5 with Me_2Zn ^[26] in pentane, according to the procedures of Fowles et al. and Jvinall, respectively.^[7] In typical experiments NbCl_5 (1.00 g, 3.7 mmol) in *n*-pentane solution was treated with ZnMe_2 (0.35 g, 3.7 mmol or 0.60 g, 6.3 mmol) to give Me_2NbCl_3 or Me_3NbCl_2 , respectively. The volatile materials were separated by vaporization and fractional condensation in vacuo in all-glass apparatus, and the purity of each was assessed by reference to the $^1\text{H NMR}$ spectrum of a CD_2Cl_2 solution^[7] and to the IR spectrum of the annealed solid condensate at -196°C .^[27] NMR spectra were recorded by using a Bruker AM500 MHz spectrometer. IR spectra of solid films and of solid N_2 matrices doped with Me_2NbCl_3 or Me_3NbCl_2 were measured with a Perkin-Elmer 580B dispersive spectrometer with an optimal resolution of 0.5 cm^{-1} . Raman spectra were recorded for solutions in CCl_4 and C_6H_6 using a Perkin-Elmer 1700X FT-Raman spectrometer at a resolution of 4 cm^{-1} . Samples for electron diffraction were sealed in glass ampoules and stored at -196°C until required.

Gas electron diffraction data were recorded on the Balzers KGD-2 unit at the University of Oslo.^[28] Experimental conditions and data processing details are summarized in Table 1 and in the Supporting Information.

Crystallographic data for Me_3NbCl_2 at 193 K: $M_r=208.91$; space group $P6_3mc$ (Int. Table No. 186), $a = 7.4356(5)$, $c = 8.1081(5)\text{ \AA}$, $V = 388.22(4)\text{ \AA}^3$; $Z=2$, $F(000)=204$, $\rho_{\text{calcd}} = 1.787\text{ g cm}^{-3}$, $\mu = 21.3\text{ cm}^{-1}$. Detailed information on data reduction and refinements, fractional atomic coordinates and mean square atomic displacement parameters are presented in the Supporting Information.

CCDC-246742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations on Me_3NbCl_2 , Me_2NbCl_3 and several benchmark systems were carried out in GAUSSIAN03 and GAUSSIAN98.^[29] The B3LYP/DZVP computational level^[30-32] will be our default in the following. The

Table 1. Gas electron diffraction measurements on Me_3NbCl_2 and Me_2NbCl_3 .

	Me_3NbCl_2		Me_2NbCl_3	
camera distance [mm]	498.8	248.9	498.7	248.9
nozzle temperature [°C]	44 ± 2	48 ± 2	21 ± 2	44 ± 2
number of plates	6	6	5	6
<i>s</i> range [Å ⁻¹]	1.750–15.250	3.500–30.000	1.750–15.125	3.500–30.000
Δs [Å ⁻¹]	0.125	0.250	0.125	0.250

built-in NBO code of the GAUSSIAN98 program was used for the construction of orthonormal natural bond orbitals (NBOs).^[33] Topological analyses of theoretical charge densities were performed with the program system AIMAC^[34] and the NBO2WFN conversion routine developed by one of us (D.S.). The solid-state structure of Me_3NbCl_2 was optimized at the PBE/PBE/LANL2DZ computational level^[35,36] with the periodic boundary condition algorithm of Kudin and Scuseria^[37] implemented in GAUSSIAN03.

Results

Vibrational spectra: For a pentacoordinated system $\text{Me}_n\text{MCl}_{5-n}$ ($n=2$ or 3) centered on a M atom formally possessing a 10-electron valence electron count, the VSEPR model predicts a TBP configuration with the more electro-negative Cl substituents occupying axial positions. This will give the C_2NbCl_3 skeleton of Me_2NbCl_3 C_{2v} symmetry, with stretching vibrations that span the representation $3a_1 + 1b_1 + 1b_2$. The C_3NbCl_2 skeleton of Me_3NbCl_2 will on the other hand have D_{3h} symmetry with the vibrational representation $2a_1' + 1a_2'' + 1e'$ for the stretching modes. The internal vibrations of the methyl groups, which resemble closely those reported for the molecules MeTiCl_3 ^[38] and Me_2TiCl_2 ^[39] are unlikely to be useful reporters on the skeletal geometries of the molecules.

Assignment of the skeletal fundamentals was assisted by reference to the vibrational spectra reported previously for NbCl_5 ,^[40] Me_2AsCl_3 ^[41] and Me_3AsCl_2 ,^[42] by the response of the different bands to deuteration of the methyl groups; and by the depolarization ratios of the Raman bands of the molecules in solution. In the event, we find that the IR spectrum of Me_2NbCl_3 isolated in an N_2 matrix contains at least four absorptions, two (at 340 and 382 cm^{-1}) attributable to $\nu(\text{Nb}-\text{Cl})$ and two (at 413 and 511 cm^{-1}) attributable to $\nu(\text{Nb}-\text{C})$ modes. By contrast, the IR spectrum of Me_3NbCl_2 under similar conditions shows only one absorption of each type (at 375 and 518 cm^{-1} , respectively). These results are totally consistent with the selection rules expected to operate for molecular frameworks with the highest possible symmetries of C_{2v} and D_{3h} , respectively.

Choice of models—DFT calculations: The vibrational spectra of Me_3NbCl_2 imply axial siting of the Cl atoms, with D_{3h}

symmetry for the heavy-atom skeleton. With due allowance for the orientations of the CH_3 groups in the equatorial plane, the molecule may then be represented by models with either C_{3h} or C_{3v} symmetry. The C_{3h} model is characterized by a horizontal mirror plane so that the

NbC_3 unit must lie in this plane together with one H atom of each CH_3 group, and the two Nb–Cl distances must be equal. The C_{3v} model (Figure 1b) can be derived from the

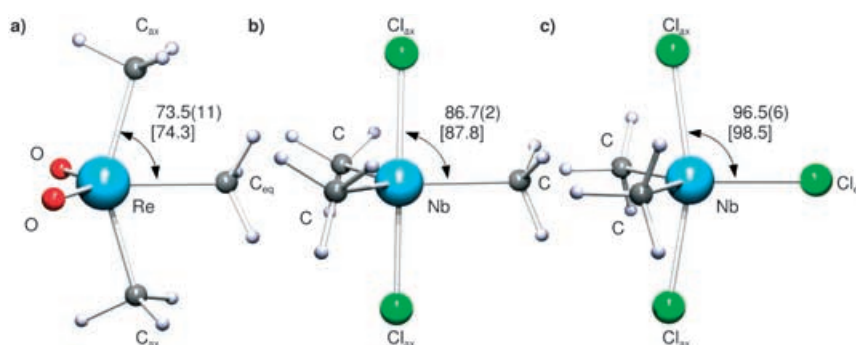


Figure 1. Molecular models of a) Me_3ReO_2 , b) Me_3NbCl_2 , and c) Me_2NbCl_3 characterized by C_s , C_{3v} , and C_{2v} symmetries, respectively. Salient valence angles [°] are specified and compared with the calculated values (in square brackets).

C_{3h} one by rotating all the CH_3 groups through 30° in a clockwise sense so that one C–H bond in each CH_3 group eclipses the same Nb–Cl bond. Since this model does not imply any horizontal mirror plane, it admits the possibilities i) that the Nb–Cl distances are different, and ii) that the ClNbC angles deviate from 90°. Such a model is indeed stabilized by 1 kJ mol^{-1} in the DFT calculations in comparison with the C_{3h} model; the Nb–Cl bond lengths differ slightly (by 0.012 Å) with the eclipsed Nb–Cl bond being the shorter, and subtending a ClNbC angle of 92.2°. In addition, three imaginary frequencies for methyl group rotation ($a'' = -65.6$, $e'' = -65.0$, -65.0 cm^{-1}) classify the C_{3h} model as a transition state on the potential energy surface between two forms of the minimum-energy C_{3v} geometry. We note that the C_{3v} model is in accord with the observed IR spectrum, since the skeletal fundamentals are not significantly affected by the orientation of the methyl groups in either D_{3h} or C_{3v} symmetry.

The most likely configuration for Me_2NbCl_3 is based on a TBP model but with one equatorial CH_3 group in this molecule replaced by a Cl atom. The skeletal symmetry is then C_{2v} , as indicated by the vibrational spectra of the compound. Such a geometry is endorsed by our DFT calculations which find a potential energy minimum for a structure with the two CH_3 groups oriented so as to maintain the symmetry of the skeleton, as shown in Figure 1c. With this symmetry, the axial Nb–Cl bonds are equivalent, but both the axial Cl–Nb–

Cl and equatorial C-Nb-C angles are free to deviate from the values of 180 and 120°, respectively, which would be expected for the idealized TBP model.

Further *ab initio* and DFT calculations, employing different bases on Me_3NbCl_2 , consistently returned the same findings, that is, a C_{3v} rather than a C_{3h} equilibrium structure for Me_3NbCl_2 and a C_{2v} one for Me_2NbCl_3 , with only minor changes in the relevant dimensions (see Supporting Information for further details). Investigation of a C_3 model for Me_3NbCl_2 , generated by concerted rotation of the CH_3 groups through 15° away from the C_{3v} configuration, showed persistent convergence back to the C_{3v} structure at all the computational levels employed.

Structure refinements

i) Gas electron diffraction:

Analysis and refinement of the GED data were accommodated by the models described above and represented in Figure 1. In each case, the CH_3 groups were additionally restricted to having local C_{3v} symmetry and being equidimensional, in keeping with the results of the DFT calculations. Hence the C_{3h} model for Me_3NbCl_2 is described by four independent parameters [the distances Nb-Cl, Nb-C, and C-H; and the angle $\angle\text{NbCH}$], while the C_{3v} model is described by six such parameters (the distances Nb-Cl_{ax}, Nb-Cl_{eq}, Nb-C, and C-H; and the angles $\angle\text{Cl}_{\text{ax}}\text{NbCl}_{\text{eq}}$, $\angle\text{CNbC}$, and $\angle\text{NbCH}$). The C_{2v} model for Me_2NbCl_3 is described by seven parameters:

the distances Nb-Cl_{ax}, Nb-Cl_{eq}, Nb-C, and C-H; and the angles $\angle\text{Cl}_{\text{ax}}\text{NbCl}_{\text{eq}}$, $\angle\text{CNbC}$, and $\angle\text{NbCH}$. The DFT calculations permitted vibrational correction terms to be included for Me_2NbCl_3 and Me_3NbCl_2 (C_{3v}) but not for Me_3NbCl_2 (C_{3h}) with its three imaginary vibrational frequencies. The refinements proceeded smoothly for a total of 17, 17 and 18 parameters (excluding scale factors) for Me_3NbCl_2 (C_{3h}), Me_3NbCl_2 (C_{3v}) and Me_2NbCl_3 (C_{2v}), respectively. The difference Δr between the axial Nb-Cl bond lengths in the C_{3v} model of Me_3NbCl_2 and the C-C amplitude in the C_{2v} model of Me_2NbCl_3 could not be refined independently. For the purposes of the GED analysis, the magnitudes of these two parameters were therefore set equal to the values indicated by the DFT calculations. The optimum values of salient parameters are presented in Table 2 for Me_3NbCl_2 and Table 3 for Me_2NbCl_3 . In addition to the seven vibrational amplitudes listed for Me_3NbCl_2 (C_{3v}) in Table 2, we refined

four non-bonded Cl...H amplitudes as independent parameters; the three C...H amplitudes were refined with constant differences. However, these amplitudes were determined with large uncertainties and are therefore not included in Table 2. For Me_3NbCl_2 (C_{3h}) we refined, in addition to the seven vibrational amplitudes listed in Table 2, three Cl...H and three C...H amplitudes as independent parameters, the remaining C...H amplitude being fixed at the estimated value of 0.20 Å. In total, 11 vibrational amplitudes were refined for Me_2NbCl_3 (Table 3). Molecular scattering intensities and radial distribution curves are displayed in Figure 2.

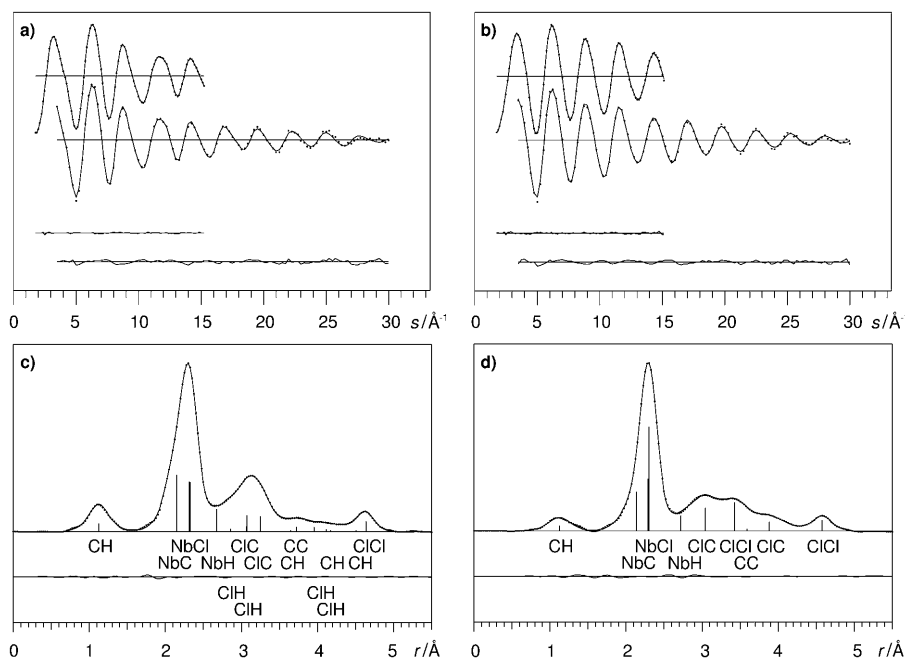


Figure 2. a)–b): upper part: experimental (dots) and calculated (solid line) modified molecular intensity curves of a) Me_3NbCl_2 and b) Me_2NbCl_3 ; below: difference curves. c)–d): upper part: experimental (dots) and calculated (solid line) radial distribution curves of c) Me_3NbCl_2 and d) Me_2NbCl_3 . Artificial damping constant $k = 0.0025 \text{ \AA}^2$; below: difference curves.

The GED analysis gives results which are consistent with the models of Me_3NbCl_2 and Me_2NbCl_3 depicted in Figure 1. The axial positions of the Cl atoms in a TBP framework are at once confirmed by the distinct peak near 4.6 Å in each of the radial distribution curves attributable to scattering from the Cl_{ax}...Cl_{ax} atom pairs (see Figure 2). Less agreement is found between some of the dimensions determined experimentally and those computed by our DFT methods; the calculated Nb-Cl distances appear systematically longer than the experimental ones. We believe the GED results to be the more reliable and the discrepancies to arise primarily from deficiencies of the DFT approximations.

For Me_3NbCl_2 , it may be noted, the GED analysis shows a marginal preference for the C_{3h} rather than the C_{3v} model ($R = 3.9$ vs 4.0%), although vibrational corrections have been included in one case but not the other. This contrasts with the outcome of the DFT calculations favoring, also

Table 2. Structural parameters and r.m.s. vibrational amplitudes as obtained from GED and quantum chemical calculations for Me_3NbCl_2 under C_{3h} and C_{3v} symmetries. Standard deviations in parentheses in units of the last digit. Distances in Å; angles in degrees.

Parameter	C_{3h}		C_{3v}	
	GED	B3LYP/DZVP	GED	B3LYP/DZVP
bond length	r_a	r_e	r_a	r_e
Nb–Cl	2.318(3)	2.369	2.319(3) ^[a]	2.370 ^[a]
Δr ^[b]	[0.000] ^[c]	[0.000] ^[c]	[0.012] ^[d]	0.012
Nb–C	2.148(4)	2.174	2.152(4)	2.173
C–H	1.119(5)	1.096 ^[a,e]	1.124(5)	1.096 ^[a,f]
valence angle	χ_a	χ_e	χ_a	χ_e
χ NbCH	108(3)	109.4 ^[a,e]	105.2(8)	109.3 ^[a,f]
χ ClNbC	[90.0] ^[c]	[90.0] ^[c]	93.3(2)	92.2
χ CNbC	[120.0] ^[c]	[120.0] ^[c]	119.7(1)	119.9
vibrational amplitude l				
Nb–Cl	0.064(2)		0.061(2)	0.054 ^[a]
Nb–C	0.086(6)		0.078(6)	0.059
C–H	0.068(6)		0.072(7)	0.077 ^[a]
Nb...H	0.20(3)		0.22(2)	0.142 ^[a]
C...C	0.14(2)		0.16(2)	0.127
Cl...C	0.145(4)		0.09(1)	0.145 ^[a]
Cl...Cl	0.075(7)		0.078(7)	0.070
R ^[g] [%]	3.9	–	4.0	–

[a] Mean value. [b] $\Delta r = r(\text{Nb–Cl}') - r(\text{Nb–Cl}'')$. [c] Parameter constrained by symmetry. [d] Fixed value. [e] Individual bond lengths and valence angles are: C–H 1.099 Å (1×) and 1.094 Å (2×); χ NbCH 106.3° (1×) and 110.9° (2×). [f] Individual bond lengths and valence angles are: C–H 1.093 Å (1×) and 1.097 Å (2×); χ NbCH 111.0° (1×) and 108.5° (2×). [g] $R = [\sum W(I_{\text{obs}} - I_{\text{calcd}})^2 / \sum W I_{\text{obs}}^2]^{1/2}$.

Table 3. Structural parameters and r.m.s. vibrational amplitudes as obtained from GED and quantum chemical calculations for Me_3NbCl_3 under C_{2v} symmetry. Standard deviations in parentheses in units of the last digit. Distances in Å; angles in degrees.

Parameter	GED	B3LYP/DZVP
bond length	r_a	r_e
Nb–Cl _{ax}	2.304(5)	2.361
Nb–Cl _{eq}	2.288(9)	2.321
Nb–C	2.135(9)	2.180
C–H	1.12(1)	1.094 ^[a,b]
valence angle	χ_a	χ_e
χ Cl _{ax} NbCl _{eq}	96.5(6)	98.5
χ Cl _{ax} NbC	86.5(3)	85.8
χ CNbC	114(2)	121.0
χ NbCH	109(2)	108.9 ^[a,b]
vibrational amplitude l		
Nb–Cl _{ax}	0.07(1)	0.052
Nb–Cl _{eq}	0.05(1)	0.048
Nb–C	0.13(1)	0.059
C–H	0.09(1)	0.076 ^[a]
Nb...H	0.17(4)	0.139 ^[a]
C...C	[0.130] ^[c]	0.130
Cl _{ax} ...C	0.14(1)	0.126
Cl _{eq} ...C	0.13(1)	0.137
Cl _{ax} ...Cl _{eq}	0.16(1)	0.132
Cl _{ax} ...Cl _{ax}	0.084(9)	0.077
R ^[d] [%]	3.8	–

[a] Mean value. [b] Individual bond lengths and valence angles are: C–H 1.099 Å (1×) and 1.092 Å (2×); χ NbCH 106.3° (1×) and 110.2° (2×). [c] Fixed value. [d] $R = [\sum W(I_{\text{obs}} - I_{\text{calcd}})^2 / \sum W I_{\text{obs}}^2]^{1/2}$.

marginally, the C_{3v} model. A similar indeterminate situation arises in the case of Me_3AsCl_2 , a C_{3v} model of which yields a lower energy than a C_{3h} one in an HF study, while GED results come out with a slight preference for the latter model.^[13] Whatever the symmetry of the equilibrium struc-

ture may be, it seems clear that the barrier to concerted internal rotation of the three methyl groups of both molecules is smaller than the thermal energy at the temperature of the GED experiments (namely $RT = 2.5 \text{ kJ mol}^{-1}$ at room temperature). For most molecules in the molecular beam, this means virtually unhindered internal rotation of the methyl groups. In order to secure further evidence for the postulated distortions of Me_3NbCl_2 in the C_{3v} DFT model, we have performed an X-ray study on a single crystal of Me_3NbCl_2 .

ii) X-ray diffraction: Crystals of Me_3NbCl_2 were found to consist of essentially discrete Me_3NbCl_2 molecules. The final model of Me_3NbCl_2 deduced from our X-ray diffraction ex-

periment at 193 K is presented in Figure 3a along with salient structural parameters. The Me_3NbCl_2 molecules display a hexagonal close packing arrangement (NiAs-type) without significant intermolecular interactions. Hence, the structural parameters of Me_3NbCl_2 in the solid state are in good agreement with those determined in the gas phase by GED and DFT calculations. In both states C_{3v} models with pyramidal Me_3Nb structures result. The structural distortion of the Me_3Nb fragment is further supported by periodic DFT optimization of the solid state structure^[43] of Me_3NbCl_2 ; the deviations from C_{3h} symmetry are clearly signaled by the Cl1–Nb–C angle with an average value of 92.7° for the DFT model (Figure 3b) in close agreement to the experimental one of 93.7(7)°. Hence a consistent picture emerges from experimental and theoretical studies in the solid and gas phases: the NbC_3 skeleton displays a slightly pyramidal structure.

Comparison with related molecules: In Table 4 we compare the dimensions determined for Me_2NbCl_3 and Me_3NbCl_2 with those reported in the literature for other TBP molecules of Groups 5 and 15. Several features relating to the structure and bonding of TM and main group TBP molecules are revealed, as discussed below.

A recent reinvestigation of the gaseous NbCl_5 molecule on the basis of GED and high-level quantum chemical studies showed it to possess a TBP skeleton with D_{3h} symmetry and axial and equatorial Nb–Cl bonds measuring 2.306(5) and 2.275(4) Å, respectively.^[44] These come close to the dimensions we have found for the corresponding bonds in Me_2NbCl_3 [2.304(5)/2.288(9) Å]. Me_3NbCl_2 invites comparison with the analogous tantalum compound. On the evi-

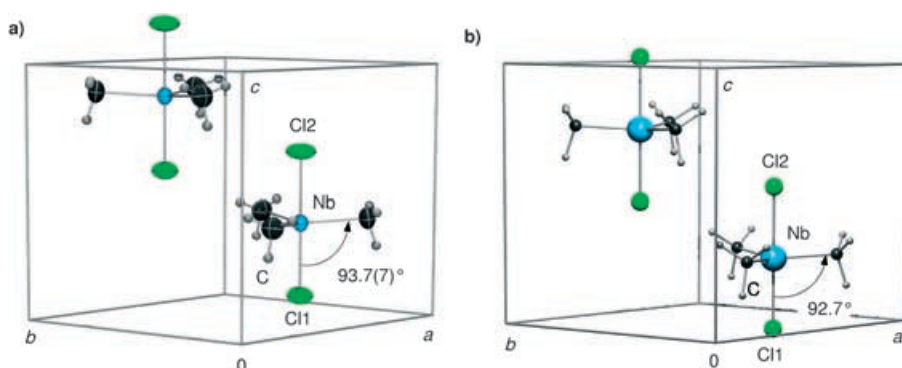


Figure 3. Molecular model and unit cell dimensions of Me_3NbCl_2 as obtained by a) X-ray diffraction at 193 K (ORTEP representation at 50% probability level) and b) by DFT calculations employing periodic boundary conditions (PBC) and simultaneous optimization of the molecular geometry and translational vectors (PBEPBE/LANL2DZ). Bond lengths [Å] and valence angles [°] (calculated average values in square brackets): Nb–Cl1 2.358(7) [2.419]; Nb–Cl2 2.285(8) [2.417]; Nb–C 2.133(5) [2.139]; \angle Cl1–Nb–C 93.7(7) [92.7]; \angle Cl2–Nb–C 86.3(7) [87.3]; \angle C–Nb–C 119.6(17) [119.8]; note that two independent Me_3NbCl_2 molecules per unit cell were optimized in the solid by the PBC calculations without any symmetry restraints. However, the final geometries of both molecules closely conform to local C_{3v} symmetry (as in the experimental structure) and both molecules are related by symmetry. See Supporting Information and ref. [43] for further information.

dence of its GED pattern,^[10] Me_3TaCl_2 is also a TBP molecule with skeletal bond lengths, Ta–Cl_{ax} 2.317(3) and Ta–C_{eq} 2.158(5) Å, very close to the corresponding distances of the niobium compound [namely Nb–Cl_{ax} 2.319(3) and Nb–C_{eq} 2.152(4) Å for the C_{3v} model]. This similarity provides yet another manifestation of the lanthanide contraction.

For species of the type $\text{Me}_n\text{MX}_{5-n}$ ($M = \text{P, As, or Sb}$; $X = \text{halogen}$), both $r(\text{M–C})$ and $r(\text{M–X})$ increase with increasing value of n . Any similar trend for the derivatives of niobium and tantalum appears much less marked. Further-

more, the difference in the lengths of axial and equatorial bonds, $\Delta r = r(\text{M–X}_{\text{ax}}) - r(\text{M–X}_{\text{eq}})$, depends strongly on whether M is a Group 5 or a Group 15 element. In the former case, values of Δr are found in the range 0.00–0.05 Å, whereas in the latter Δr spans the range 0.05–0.10 Å, the last value representing a 5% difference (in the P–Cl bonds of PCl_5 ^[45]). This familiar behavior of the Group 15 derivatives has been rationalized in terms of the effective electronegativity of the central atom and the hypervalent nature and consequent orbital deficiency of the molecule, implying a significant difference in polarity between axial and equatorial M–X

bonds.^[46] By contrast, the Group 5 derivatives have no such problem of orbital deficiency in accommodating bonding electron density; if anything, they are electron-deficient, at least with regard to the 18-electron rule.^[47]

In both Me_2NbCl_3 and Me_3NbCl_2 , the methyl groups occupy exclusively equatorial sites, with the chloro ligands filling the remaining positions. In this respect at least, they resemble the phosphoranes Me_2PF_3 and Me_3PF_2 .^[4,5] An interesting contrast with Me_3NbCl_2 is provided, though, by Me_3ReO_2 ,^[25] which can be formally derived from the niobi-

Table 4. Comparison of structural parameters of some pentacoordinate derivatives of the halides of transition and main group elements. Distances in Å; angles in degrees.

Molecule	$r(\text{M–C}_{\text{eq}})$	$r(\text{M–X}_{\text{ax}})$	$r(\text{M–X}_{\text{eq}})$	\angle CMC	\angle X _{ax} MX _{eq}	Method	Ref.
Group 5							
VF_5		1.734(7)	1.708(5)		[90.0] ^[a]	GED	[64]
NbCl_5		2.306(5)	2.275(4)		[90.0]	GED	[44]
Me_2NbCl_3	2.135(9)	2.304(5)	2.288(9)	114(2)	96.5(6)	GED	[b]
Me_3NbCl_2	2.152(4)	2.319(3) ^[d]		119.7(1)		GED	[b,c]
Me_3NbCl_2	2.133(5)	2.322(8) ^[d]		119.6(17)		X-ray	[b]
Me_3TaF_2	2.125(5)	1.863(4)		[120.0]		GED	[9]
TaCl_5		2.313(5)	2.266(4)		[90.0]	GED	[1]
Me_3TaCl_2	2.158(5)	2.317(3)		[120.0]		GED	[10]
Group 15							
PF_5		1.577(5)	1.534(4)		[90.0]	GED	[65]
Me_2PF_3	1.798(4)	1.643(3)	1.553(6)	124.0(8)	88.9(3)	GED	[4]
Me_3PF_2	1.813(1)	1.685(1)		[120.0]		GED	[5]
PCl_5		2.125(3)	2.021(3)		[90.0]	GED	[45]
AsF_5		1.711(5)	1.656(4)		[90.0]	GED	[66]
Me_3AsF_2	1.897(6)	1.820(6)		[120.0]		GED	[67]
AsCl_5		2.207(1)	2.113(1) ^[d]		89.98(2) ^[d]	X-ray	[68]
Me_3AsCl_2	1.925(2)	2.349(3)		[120.0]		GED	[13]
Me_3SbF_2	2.091(3) ^[d]	1.999(3) ^[d]		120.0(1) ^[d]		X-ray	[69]
SbCl_5		2.338(7)	2.277(5)		[90.0]	GED	[70]
SbCl_5		2.333(2)	2.270(2)		[90.0]	X-ray	[68]
Me_3SbCl_2	2.107(6)	2.460(6)		[120.0]		GED	[71]

[a] Values constrained by symmetry. [b] This work. [c] For C_{3v} model (see text). [d] Mean value (standard deviations for averaged solid-state structure parameters were obtained by the error propagation method).

um compound by replacing the weak π -donor chloro ligands by strongly π -donating oxo ligands at the Group 7 metal center (Figure 1a). In this case, both oxo ligands occupy equatorial sites, rather than the axial sites favored by the chloro ligands in Me_3NbCl_2 , in what has been described as an edge-bridged tetrahedral (EBT)^[48] structure.

More striking, however, is the case of Me_2NbCl_3 . Whereas the skeletal angles in the main group compound Me_2PF_3 conform to conventional VSEPR arguments based on the different electronegativities of the methyl and fluoro ligands [$\angle \text{F}_{\text{ax}}\text{PF}_{\text{eq}} = 88.9(3)^\circ$],^[4] those of Me_2NbCl_3 show that it has to be classified as a non-VSEPR compound. Thus, the axial Nb–Cl bonds in Me_2NbCl_3 bend *away* from, and not toward, the equatorial Nb–Cl bond; at $96.5(6)^\circ$ the angle $\angle \text{Cl}_{\text{ax}}\text{NbCl}_{\text{eq}}$ must be considered significantly larger than 90° , and this feature is also modeled by the DFT calculations. At the same time, the equatorial C–Nb–C unit closes down from 120 to $114(2)^\circ$, showing that the C atoms are pushed closer together.^[49] Such a geometry contrasts with the normal VSEPR forecasts to the effect that the bonds to the less electronegative ligands have larger spatial requirements on the surface of the central atom and thus span a larger angle.^[3] The observed structure is not unprecedented, however, for the AX_2Y_2 molecule Me_2TiCl_2 one finds the Ti–Cl bonds spanning not the smallest but the largest angle, with $\angle \text{ClTiCl} = 117.3(3)$, $\angle \text{ClTiC} = 108.9(2)$, and $\angle \text{CTiC} = 102.8(9)^\circ$,^[17] an anomaly that cannot be explained by steric congestion of the individual M–C and M–Cl electron pair domains.

It is clear that other factors not accounted for by the classical VSEPR model are at work in determining the geometry of Me_2NbCl_3 . Accordingly, we have carried out further DFT calculations to explore the *total* pattern of electron localization at the Nb center in both Me_2NbCl_3 and Me_3NbCl_2 . The topology of the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r})$, was analyzed to reveal local charge concentrations at the metal atom likely to have a significant impact on the structures of these d^0 TM alkyl derivatives.^[20,22–24,50] To complement these studies, we outline for the first time a concept that explains the nature and occurrence of LICCs by a rigorous interpretation of the wavefunctions of Me_3NbCl_2 and Me_2NbCl_3 , which may be regarded as paradigms of heteroleptic d^0 molecules.

Discussion: LICCs and the Structures of TM Compounds

Overview: In a recent review of non-VSEPR structures, Kaupp pointed out that a complex interplay of four factors is responsible for the formation of structures which obey or violate the predictions of the VSEPR model.^[14b] In summary, core polarization and d-orbital participation in σ -bonding disfavor VSEPR arrangements, whereas ligand repulsion and π -bonding encourage such arrangements. Kaupp concluded that the structural influence of π -bonding is rather difficult to assess, since it depends not only on the π -donor

capacity of the ligands, but also in a complex way on the valence angle subtended by these ligands at the central atom. Furthermore, the type of π -bonding (namely in-plane or out-of-plane) must be identified in order to analyze its effects. To complicate matters yet further, the structural influence of π -bonding was found to depend on the coordination number of the metal center.^[14a] Within this rather labyrinthine situation, calculations may be reliable in prediction but are, as pointed out by Seppelt,^[51] rather opaque of expression in simple physical terms. Accordingly, there is a compelling need to extend a readily understood model, such as VSEPR, so as to accommodate the various factors clearly, consistently, and faithfully.

Such an extension was in fact proposed by Gillespie et al. in 1996^[52] and refined by Bader, Gillespie and Martin (BGM) in 1998.^[23] BGM proposed that a heavy central atom may be susceptible to ligand-induced polarization of the outer shell of the core—termed the “effective valence shell”. These authors further concluded that the Laplacian of the charge density, $\nabla^2\rho(\mathbf{r})$, can be used to localize LICCs^[53] as a signature of the local polarization of the central atom. They also found that the more covalent a metal–ligand bond, the larger is the *trans*-LICC induced at M diametrically opposed to it. In the BGM approach, *trans*-LICCs, along with bonding CCs (BCCs) and the ligands themselves, each make spatial demands at the central atom; the global resolution of these leads to the lowest energy conformation that may or may not agree with the predictions of the simple VSEPR theory. However, there has been no consensus on this point or on other simplified explanations^[51,54] that have been advanced, since the precise significance of the LICCs has remained unclear. Not without reason Seppelt has contended^[51] that these features have not been observed experimentally and are merely the creatures of sophisticated computational methods.

Herein we demonstrate a solution to these inadequacies. In a study by Scherer and McGrady in 2003, the existence of pronounced LICCs was confirmed *experimentally* for a TM alkyl complex, and their origin was traced to covalent metal–ligand bond formation employing metal d orbitals.^[24] In a search for further support of the extended VSEPR model, we have analyzed the wavefunctions of the present molecules Me_3NbCl_2 and Me_2NbCl_3 by a combined study employing both MO- and charge-density-based methods.

The nature and origin of LICCs: We first consider the simplest model system which displays covalent bonding between a TM and a ligand, namely CaH^+ . The charge density contours of the natural bond orbital (NBO) representing the $\sigma(\text{Ca-H})$ bond are depicted in Figure 4 in juxtaposition to the σ -bonding NBO of its main group congener MgH^+ . According to an NBO analysis, the Ca–H bond shows 20.2% metal character, indicative of significant covalent bonding employing $sd^{0.67}$ hybridization at the Ca atom (59.6% 4s- and 40.0% $3d_{z^2}$ character). The overall p-type contribution amounts to a mere 0.4% for the $\sigma(\text{Ca-H})$ NBO making

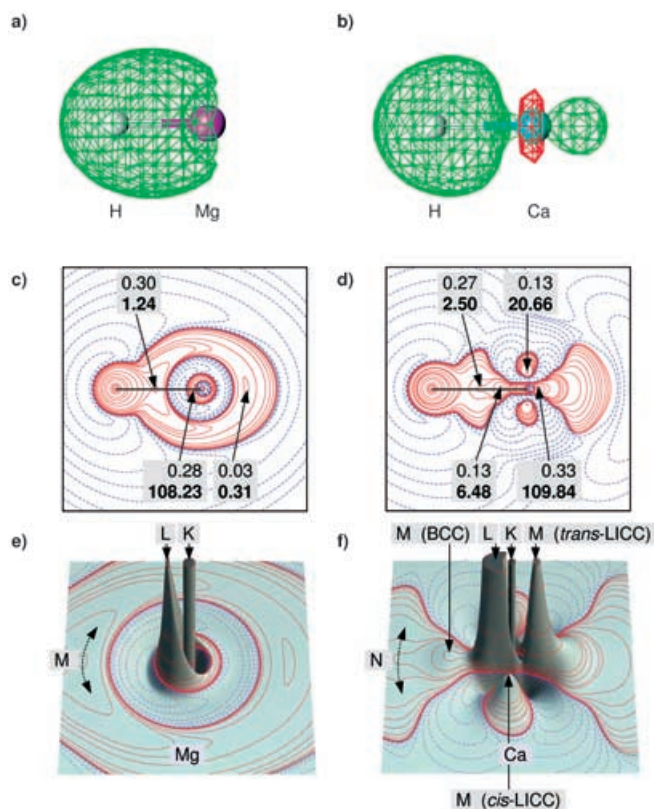


Figure 4. Constant probability density surfaces for bonding NBOs of a) MgH⁺ and b) CaH⁺, with corresponding contour (c, d) and relief plots (e, f) of the negative Laplacian of charge densities of the NBOs, $L(r)$, in a plane containing the metal–hydrogen directrix of MgH⁺ (left) and CaH⁺ (right). Default contour values equal $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n \text{ e } \text{Å}^{-5}$, where $n=0, -3, \pm 2, \pm 1$; positive and negative values of $L(r)$ are marked by red solid and blue dashed lines, respectively. The relief plots are truncated at $100.0 \text{ e } \text{Å}^{-5}$ for the sake of clarity. Extra contour lines at 1.23, 0.30 (c, e) and 2.45, $6.00 \text{ e } \text{Å}^{-5}$ (d, f) are drawn to reveal relative positions of the LICCs; $\rho(r)$ values in $\text{e } \text{Å}^{-3}$; $L(r)$ values are listed in bold in $\text{e } \text{Å}^{-5}$.

CaH⁺ the simplest and therefore optimal testbed for analyzing the origin and nature of LICCs in d⁰ TM compounds.

In Figure 5a,b the total charge densities, $\rho(r)$, of MgH⁺ and CaH⁺ are shown as relief maps which reveal hardly any features hinting at significant metal polarization. In the case of the TM model, CaH⁺, however, the Laplacian of the charge density, $\nabla^2\rho(r)$, displays clearly a polarization of the metal center^[55] in the profile of $\nabla^2\rho(r)$ along the Ca–H bond (Figure 5d), and also in the corresponding relief map and isosurface map at a constant $\nabla^2\rho(r)$ value of $-71.0 \text{ e } \text{Å}^{-5}$ (Figure 5f). Hence the Laplacian as a localization function reveals a BCC at the Ca atom facing the hydrogen ligand, and a *trans*-LICC diametrically opposite. In addition to these two charge concentrations, a third one forming a belt around the Ca atom is denoted *cis*-LICC. According to the NBO analysis, any contribution by natural p-AO functions to the $\sigma(\text{Ca–H})$ NBO is marginal. Hence the ligand-induced polarization of the cation must be directly related to the contribution of the 3d_{z²} AO to the total charge density. This can be demonstrated in greater detail

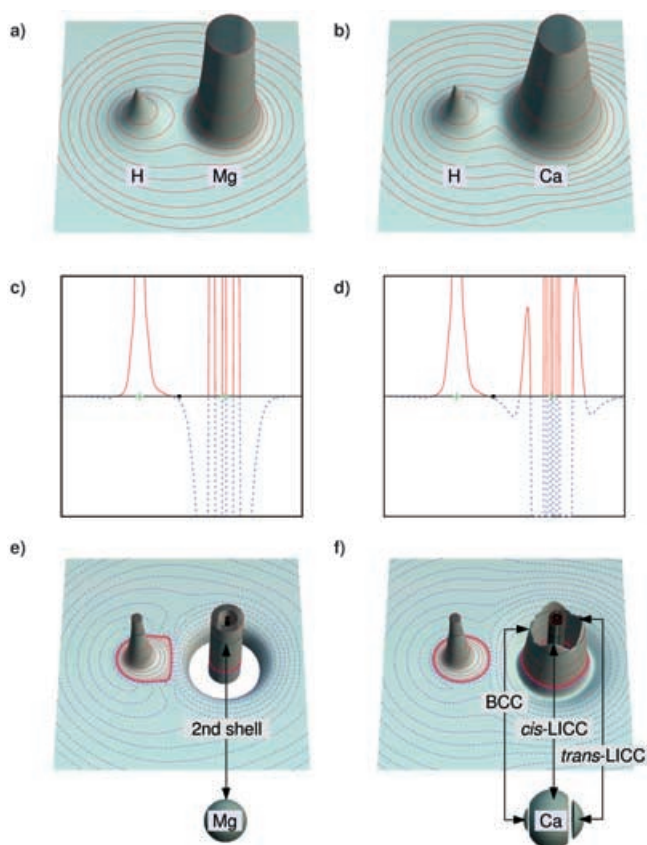


Figure 5. Relief plots of total charge densities of a) MgH⁺ and b) CaH⁺, $\rho(r)$, in a plane containing the metal–hydrogen directrix. Default contour values equal $\pm 2.0 \times 10^n$, $\pm 4.0 \times 10^n$, $\pm 8.0 \times 10^n \text{ e } \text{Å}^{-3}$, where $n=0, -3, -2, \pm 1$. The plots are truncated at $6.0 \text{ e } \text{Å}^{-3}$ for the sake of clarity. Below: corresponding bond profiles (c, d), relief, and isosurface plots (e, f) of the negative Laplacian of $\rho(r)$ of MgH⁺ (left) and CaH⁺ (right). Default contour values and cut-offs as defined in Figure 4c–f were used. Nuclei and BCCs are denoted with closed black circles and green crosses, respectively. Black solid lines on the relief plots (e, f) correspond to the isovalue (envelope) surfaces of $L(r)$ drawn at $71.0 \text{ e } \text{Å}^{-5}$ and presented in the respective insets.

by analysis of the individual contribution of the $\sigma(\text{Ca–H})$ NBO to the total charge density: the Laplacian of the σ -NBO density contours (Figure 4c–f)^[56] of our models CaH⁺ and MgH⁺ reveals all the essential features that characterize the nature of the LICCs, as set out below.

i) All three or four quantum shells of the Mg and Ca atoms, respectively, are resolved in the $\nabla^2\rho(r)$ relief map of the charge density of the corresponding σ -NBOs. Closer inspection of Figure 4e, f shows the M shell of the Mg cation and the N shell of Ca cation to be rather indistinct, in agreement with the relatively diffuse character of the 3s and 4s atomic functions, and the cationic nature of both metals in MgH⁺ and CaH⁺. As a consequence, this weak undulation is damped out in the Laplacian of the total charge density. Accordingly, only three shells are resolved for the Ca atom when the total charge density is analyzed (Figure 5). In this respect, Ca

shows the same incomplete shell structure as a regular transargonic element: the $(n-1)$ quantum shell is not revealed in the Laplacian. Nevertheless, careful analysis of the Laplacian along the Ca–H directrix still reveals a point of inflection (Figure 5d). This point coincides with the region of the fourth quantum shell, when only the charge density contribution of the σ -NBO of CaH^+ is taken into account. Hence it may be considered as the residual echo of the fourth quantum shell of Ca.^[57] This result clearly underlines the success of our concept for analysis not only of the total charge density, $\rho(\mathbf{r})$, but also of its individual contributions to the underlying NBOs. Hence, partitioning of the charge density via the NBO methods appears to provide a new and detailed insight into the electronic structures of compounds.

- ii) As a spin-off of this approach, we can now visualize how the ligand in each of our benchmark systems induces a clear polarization of the inner core shells of the metal. In MgH^+ (Figure 4c,e), the charge concentration of the L shell is clearly polarized toward the hydrogen ligand: the ligand-opposed rear side of the L shell of charge concentrations is substantially depleted. In the case of the more covalent CaH^+ ,^[58] the core polarization is even more pronounced: the corresponding rear side of the L shell of charge concentration in Figure 4f is completely depleted, and displays a positive value of $\nabla^2\rho(\mathbf{r})$. The remaining polarization features can now be assigned to the remnants of the N shell (denoted by a broken line) and the characteristic polarization pattern of the M shell which is less pronounced but still recovered in the global polarization pattern of the total charge density of CaH^+ (Figure 5f). According to the character of the σ NBO of CaH^+ —composed of 4s and $3d_{z^2}$ natural atomic orbitals (NAOs) at the Ca atom—the existence of the BCC and LICC in the M shell of charge concentration at the Ca atom can now be clearly ascribed to the contribution of the $3d_{z^2}$ NAO function at Ca (Figure 5f). As a consequence, it is the nodal structure of the $3d_{z^2}$ NAO which is ultimately responsible for the formation of the diffuse belt denoted *cis*-LICC, as well as for the BCC and the *trans*-LICC, and hence for the polarization of the Ca cation (Figure 5f). Most chemists concur that the 4s and 3d orbitals of a first-row TM are its valence orbitals. Accordingly, we prefer to avoid the potentially confusing terms “core charge concentrations” or “charge concentrations of the outermost core” introduced by Gillespie^[20,52] and Bader^[22,50] and to use instead “valence shell charge concentrations”, or simply “charge concentrations” (CCs), for both main-group and TM compounds.
- iii) In the final step of our analysis, we consider whether the pronounced *trans*-LICC seen in CaH^+ might arise from use of Ca p functions in the bonding. To address this question, we have analyzed the electronic situation in the lighter congener MgH^+ (Figure 4c,e). The NBO of MgH^+ can be classified as a $\sigma(\text{Mg}-\text{H})$ bonding orbital with the characteristics typical of a main-group hydride (97.7% s- and 2.3% p-character at the Mg cation). In

contrast to its heavier congener, the polarization at the metal is now solely accomplished by p functions, which induce dipolar polarization of the metal cation during M–H bond formation, and thus create a more ionic Mg–H bond in comparison with CaH^+ . As a result, charge density is no longer concentrated *trans* to the Mg–H bond, and no LICC can be observed (Figure 4e). This example clearly illustrates that it is the different nodal structures of p and d wavefunctions that give rise to the different polarization patterns at the metal center. It thus follows the valence bond arguments outlined by Firman and Landis^[59] in accounting for the disfavor for valence angles of 180° typically displayed by TM compounds containing strong σ -bonding ligands. Figure 6a,b shows the deformation densities of MgH^+ and CaH^+ in support of our conclusion: in the case of the second short period metal Mg, a basically dipolar polarization is observed, while the first long period metal Ca displays a complex polarization pattern. Figure 6 elegantly reveals the fundamental difference between these two metals that may be traced to the ability of Ca to form sd-hybrid orbitals.

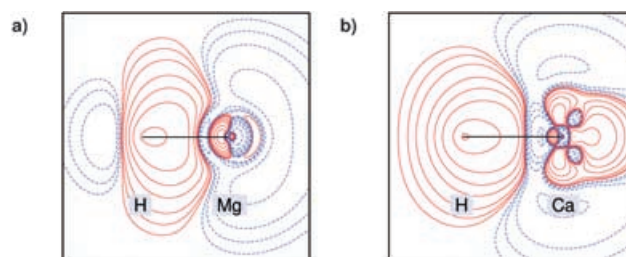


Figure 6. Deformation densities of a) MgH^+ and b) CaH^+ , $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r})_{\text{total}} - \rho(\mathbf{r})_{\text{promolecule}}$, in a plane containing the metal–hydrogen directrix; the promolecule density, $\rho(\mathbf{r})_{\text{promolecule}}$, is the superposition of charge density of spherical ground-state atoms centered at the nuclear position. Default contour values as defined in Figure 5a, b were used. Extra contour lines at $\pm 100.0 \text{ e}\text{\AA}^{-3}$ were added; positive and negative values of $\Delta\rho(\mathbf{r})$ are marked by red solid and blue dashed lines, respectively.

In the next section we will demonstrate that it is this greater orbital flexibility that allows d^0 TM compounds to adopt non-VSEPR structures. Our partitioning of the total charge density in the benchmark systems CaH^+ and MgH^+ using the NBO method may then offer the last word in a long and controversial debate on the nature and origin of local charge concentrations at TM centers. These concentrations arise from polarization of the valence electrons, and are induced by covalently bonded σ and π ligands. They are an integral part of the bonds formed using metal orbitals possessing d character. It is not surprising therefore that they contain all the information necessary to refine the VSEPR model without increasing its complexity.

Non-VSEPR geometries of Me_3NbCl_2 and Me_2NbCl_3 : In the case of simple diatomic molecules such as CaH^+ or MgH^+ ,

dissection of the charge density was straightforward since the effect of the covalent M–H bonding on the total charge density could be attributed to a single NBO. We now show that a similar partitioning of the charge density into the individual contributions of all the σ -type NBOs can be applied to more complex TM compounds. In the case of Me_3NbCl_2 and Me_2NbCl_3 , all $\sigma(\text{Nb}-\text{C})$ and $\sigma(\text{Nb}-\text{Cl})$ NBOs have been analyzed with respect to formation of valence shell charge concentrations at the Nb atom.

As shown in Figure 7, all σ -type NBOs formed by the chloro and methyl ligands in Me_2NbCl_3 resemble the σ -type NBO in CaH^+ . The charge density in the $\text{Ca}-\text{H}$ bonding domain of CaH^+ resulted mainly from the overlap between the 1s AO of hydrogen and the 4s and 3d_{2z} NAOs of the metal. In Me_3NbCl_2 and Me_2NbCl_3 , bonding is mainly established by the 5s and 4d orbitals at the metal and 2p or 3p orbitals at the carbon or chlorine atoms, respectively. Hence the origin of LICCs in these systems is similar to that in CaH^+ : they arise from the characteristic shape and symmetry of a d orbital.^[60] The Laplacian of the total charge density of Me_2NbCl_3 (Figure 8b) is approximately composed of the sum of the individual σ -NBOs shown in Figure 7d–f (see Supporting Information).

We note further that BCCs at TM atoms are typically weakly—if at all—pronounced in the Laplacian of the total charge density. In the case of Me_3NbCl_2 and Me_2NbCl_3 , which display rather polarized metal–ligand bonds, no BCCs at all can be located. As a result, only the pronounced *trans*-LICCs of the individual ligands dominate as maxima or (3,–3) critical points in the negative Laplacian of the polarization pattern at niobium (Figure 8). We conclude that the polarization pattern of Me_2NbCl_3 is consonant with the picture emerging from our NBO analysis of the molecule.

Figure 8a,b shows the envelope maps of the Laplacian at $-\nabla^2\rho(\mathbf{r})=40\text{ e}\text{\AA}^{-5}$ around the central niobium atom of Me_3NbCl_2 and Me_2NbCl_3 each at the optimized geometry. In accord with the results of BGM for Me_2TiCl_2 ,^[23] the *trans*-LICCs induced by the methyl ligands, LICC(C), are in each case significantly larger than those arising from the chloro ligands, LICC(Cl). Hence it is the more covalent Nb–C bonds rather than the more ionic Nb–Cl bonds that give rise to the more pronounced LICCs. These charge concentrations are not merely polarizations of the metal valence shell then, but can be regarded as signatures of the covalent bonding. In principle, they even offer a basis for

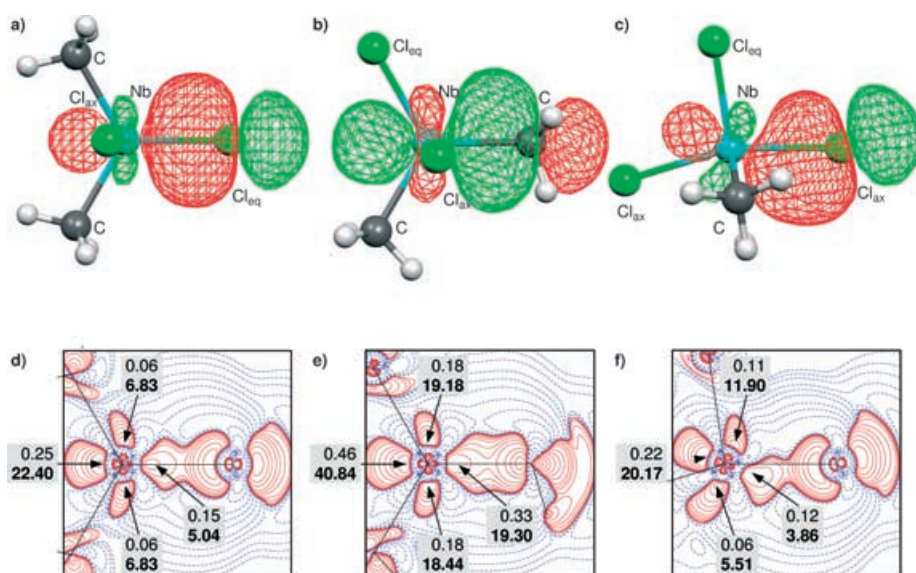


Figure 7. Constant probability density surfaces for a) Nb–Cl_{ax}, b) Nb–C, and c) Nb–Cl_{ax} bonding NBOs of Me_2NbCl_3 , with corresponding contour plots of the negative Laplacian of charge densities of the NBOs, $L(\mathbf{r})$, in C–Nb–Cl_{ax} (d, e), and Cl_{ax}–Nb–Cl_{ax} (f) planes, respectively. Default contour values as defined in Figure 4c–f were used; $\rho(\mathbf{r})$ values in $\text{e}\text{\AA}^{-3}$; $L(\mathbf{r})$ values listed in bold in $\text{e}\text{\AA}^{-5}$.

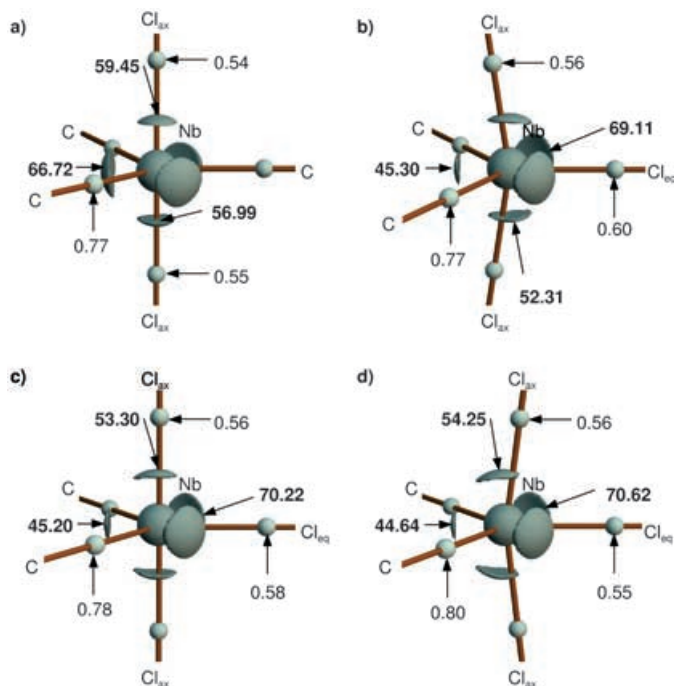


Figure 8. Isovalue surface (envelope) plots of the negative Laplacian [$L(\mathbf{r})=40\text{ e}\text{\AA}^{-5}$] for equilibrium structures of a) Me_3NbCl_2 , b) Me_2NbCl_3 , $\angle\text{Cl}_{ax}\text{NbCl}_{eq}=98.5^\circ$, and reoptimized models of Me_2NbCl_3 displaying fixed valence angles: c) $\angle\text{Cl}_{ax}\text{NbCl}_{eq}=90^\circ$ and d) $\angle\text{Cl}_{ax}\text{NbCl}_{eq}=83^\circ$; $\rho(\mathbf{r})$ values at metal–ligand BCPs (indicated by grey spheres) and $L(\mathbf{r})$ values of LICCs at the Nb atom (listed in bold) are in $\text{e}\text{\AA}^{-3}$ and $\text{e}\text{\AA}^{-5}$, respectively.

ligand (L) classification according to its capacity to form strong M–L σ bonds.

The polarization of the metal atom valence shell in the superficially more straightforward Me_3NbCl_2 is therefore do-

minated by the three pronounced *trans*-LICCs induced by the methyl groups. As a consequence, these groups adopt with the metal atom an array which is displaced by 0.083 Å from a strictly trigonal planar configuration, a scenario that results in C-Nb-C valence angles of 119.9°, close to the optimal value of 120° for the three LICC(C) features. The axial positions in Me₃NbCl₂ are then occupied by the two chloro ligands; these are mutually destabilized by the LICC(Cl) features induced *trans* to each Nb-Cl bond. Hence the axial positions are energetically less favorable and are occupied—as predicted in the simple VSEPR model—by the ligands which i) have a reduced charge density in the M-L bonding region, and ii) induce a smaller charge concentration.

The slight deviation from planarity of the NbC₃ skeleton and inequality of the axial Nb-Cl bonds characterize the C_{3v} model of the molecule which is predicted by the calculations to be its equilibrium ground state. The magnitudes of the LICCs are essentially the same for the C_{3h} as for the C_{3v} model, but the locations differ, with the preference for the C_{3v} model arising from Pauli-type repulsion between the Nb-C bonding electron pair domains and the LICC(C)s. As a consequence, the three methyl ligands and the three LICC(C)s adopt the form of a very shallow trigonal antiprism rather than a planar hexagon. Such a distortion has already been identified on the basis of IR spectra for non-VSEPR molecules such as LnMe₃ (Ln = Sc, Y, or La),^[61] which apparently display a more pronouncedly pyramidal MC₃ unit than is forecast for Me₃NbCl₂. The chloro ligands could thus be seen as inhibiting further pyramidalization of the NbMe₃ unit i) by interligand repulsion between the Nb-Cl and Nb-C bonding electron pair domains, and ii) by repulsion arising from the presence of the LICC(C)s.

Whether Pauli repulsion (favoring C_{3v} or C₃ symmetry) overcomes interligand repulsion (favoring C_{3h} symmetry) in practice we are unable to judge. However, if Pauli repulsion dominates, we are now able to predict the distortion coordinate (C_{3h} → C_{3v}) on the potential energy surface of the free molecule. Whatever the true equilibrium structure may be, the energy difference between the C_{3h} and C_{3v} forms is probably smaller than the zero point energy associated with the three CH₃ rotational modes, implying virtually unhindered internal rotation of the CH₃ groups in the gaseous molecule.

In the case of Me₂NbCl₃ (Figure 8b), the situation is more complex. Here we have to consider two different types of chloro ligand, and the molecular symmetry is reduced to C_{2v}. Once again, the LICCs induced *trans* to the methyl ligands are significantly larger than those *trans* to the axial Nb-Cl bonds; these in turn are larger than the *trans*-LICC induced by the equatorial chloro ligand, with the result that the third CC, LICC(Cl) in the equatorial plane of the molecule, is significantly smaller (ca. 45 e Å⁻⁵) than both the LICC(C)s. Hence the largest repulsion is expected between the M-C bond domains and the LICC(C)s. As a direct consequence, a χ CMC angle smaller than 120° is predicted and observed, in contrast to the expectations of the classical VSEPR model. In a similar manner, the axial positions of the chloro ligands are dictated by the dominant repulsion between the

M-Cl bond domain [ρ (M-Cl)] and the LICC(C)s. This situation leads to a χ Cl_{ax}NbCl_{eq} greater than 90°, as observed by experiment [96.5(6)°] and theory [98.5°]. Hence the extended VSEPR concept proposed by BGM^[23] accommodates the structure of Me₂NbCl₃. It is important therefore to expose the physical basis of this concept, and to test its general applicability to pentacoordinate compounds with unusual geometries.

In the final step of our analysis, a relaxed potential-energy surface (PES) scan with a varying Cl_{ax}NbCl_{eq} angle was carried out to explore how distortions away from the equilibrium geometry affect the topology of the charge density (Table 5). Figure 8c,d shows the isosurface plots of $\nabla^2\rho(r)$ at the values of χ Cl_{ax}NbCl_{eq} = 90 and 83°, respectively. Optimal bond lengths and valence angles obtained by a relaxed scan over χ Cl_{ax}NbCl_{eq} are also listed in Table 5 along with the absolute values of the LICCs obtained for each optimized geometry. The magnitudes of the LICC(C)s—and to a lesser extent the LICC(Cl_{ax})s—decrease monotonically with increasing χ Cl_{ax}NbCl_{eq}, whereas that of the LICC(Cl_{eq}) remains relatively constant. The potential energy of Me₂NbCl₃ as a function of χ Cl_{ax}NbCl_{eq} is depicted in the Supporting Information. The molecule becomes destabilized more rapidly by distortion of the equilibrium geometry toward a smaller Cl_{ax}NbCl_{eq} angle than by distortion toward a larger angle. This provides further evidence for the structure-determining role of the LICC(C)s, since smaller Cl_{ax}NbCl_{eq} angles lead to a tighter CMC angle and thus a closing of the angle formed by the corresponding LICC(C)s. Consequently the repulsion between both LICC(C)s leads to an increase of the total energy on reducing the Cl_{ax}NbCl_{eq} angle. In contrast, a widening of χ Cl_{ax}NbCl_{eq} leads to both a larger CMC angle and a larger angle between the LICC(C)s. Thus, the dominating repulsion between the LICC(C)s is reduced along this coordinate, though it is still overcompensated by increased repulsion between the Nb-C bonding electrons and the LICC(C)s, as signaled by significantly elongated Nb-C bonds.

In summary, the observed and calculated equilibrium structures of Me₂NbCl₃ and Me₃NbCl₂ are easily rationalized by taking into account the polarization of the d⁰ metal center, with Pauli repulsion between the dominant CCs induced by the covalent M-C bonds turning out to be the critical structure-determining factor.

Conclusions

The TBP structures of Me₂NbCl₃ (C_{2v}) and Me₃NbCl₂ have been confirmed experimentally and theoretically, although the overall symmetry of the latter molecule in its equilibrium ground state could not be established unequivocally. However, the X-ray model for Me₃NbCl₂ clearly indicates a slightly distorted TBP structure which does not conform with the VSEPR model but is in close agreement with the results of DFT calculations that suggest a C_{3v} geometry for the equilibrium ground state of the molecule, with one C-H

Table 5. Variation of bond lengths, valence angles and absolute values of LICCs [$-\nabla^2\rho(\mathbf{r})$] at the Nb atom in Me_2NbCl_3 (C_{2v} symmetry), as obtained from DFT scan calculations for different values of $\alpha = \angle \text{Cl}_{\text{ax}}\text{NbCl}_{\text{eq}}$. Bond lengths in Å, angles in degrees, $-\nabla^2\rho(\mathbf{r})$ values in $\text{e}\text{Å}^{-5}$.

α	Bond lengths			$\angle \text{Cl}_{\text{eq}}\text{NbC}$	Valence angles			LICCs	
	Nb–Cl _{eq}	Nb–Cl _{ax}	Nb–C		$\angle \text{Cl}_{\text{ax}}\text{NbC}$	$\angle \text{CNbC}$	(C)	(Cl _{ax})	(Cl _{eq})
83	2.385	2.363	2.156	122.3	93.7	115.5	70.62	54.25	44.64
88	2.351	2.364	2.163	121.7	91.1	116.7	70.43	53.64	45.13
90	2.343	2.364	2.167	121.4	90.0	117.2	70.22	53.30	45.20
93	2.331	2.363	2.170	120.8	88.5	118.4	69.84	52.96	45.37
98	2.319	2.361	2.178	119.5	86.1	121.0	69.12	52.39	45.41
103	2.314	2.361	2.185	117.5	84.0	125.0	68.28	51.93	45.39
108	2.313	2.361	2.189	115.1	82.5	129.8	67.37	51.63	45.19
113	2.316	2.363	2.190	112.6	81.4	134.8	66.35	51.45	44.75
118	2.322	2.365	2.188	110.3	80.6	139.5	65.29	51.27	43.99

bond of each CH_3 group eclipsing a common axial Nb–Cl bond and rendering the Nb–Cl bonds inequivalent. The structure of Me_2NbCl_3 also deviates from the predictions of the simple VSEPR model in that the expected C_{2v} geometry features axial Nb–Cl bonds that are bent *away* from rather than toward the equatorial Nb–Cl bond.

Topological analysis of total electron densities by using $\nabla^2\rho(\mathbf{r})$ as an electron localization function reveals tiny but important features of the seemingly featureless total electron density, $\rho(\mathbf{r})$, and provides a wealth of information on the polarization of charge in complex systems such as these. Analysis of the total charge density shows ligand-induced charge concentrations (LICCs) at the Nb atom to account for the non-VSEPR structures adopted, certainly by Me_2NbCl_3 and probably by Me_3NbCl_2 . In particular, the significant bending of Nb–Cl_{ax} bonds toward the C–Nb–C equatorial unit in Me_2NbCl_3 may be rationalized in terms of the mutual repulsion between bonded and ligand-opposed CCs present in the valence shell of Nb, in agreement with the extended VSEPR model suggested by BGM.^[23] However, the conventional AIM-based approach for topological analysis of the total electron density is restricted to the evaluation of “local” topological parameters at so-called critical points. This is a severe limitation, since LICCs induced by different ligands appear to have different local, as well as non-local, properties, such as shape and size. Since it is the entire distribution of charge in space that determines the equilibrium geometry of a molecule, further insight into the spatial distribution of electron density may be gained by analyzing non-local properties of the charge density, such as envelope maps of the $-\nabla^2\rho(\mathbf{r})$ function. As a result of this sort of analysis, the rather unusual structure of Me_2NbCl_3 appears to derive primarily from repulsion between the Nb–Cl_{ax} bonding electron density and the LICCs associated with the equatorial Nb–C bonds; the interactions between the Nb–Cl_{ax} bonds and their mutually disposed LICCs appear to be less important.

An important outcome of our study is the first identification of a powerful approach that explains the nature and occurrence of LICCs by a direct and rigorous interpretation of the wavefunction. All information about the origin of LICCs is directly accessible from the wavefunction via the natural bond orbital (NBO) method. In the first step of our

approach, we use the NBO method to partition the total charge density in a physically meaningful way into its individual core and valence density contributions.^[62] The valence density is thus unequivocally represented by the superposition of bonding NBOs, in agreement with the Lewis concept.^[56] In the next step, we demonstrate that all polarization features in the Laplacian of the total charge density are composed of the individual contributions from bonding NBOs. In the final step, the NBO analysis allows us to conclude that LICCs arise from polarization of the valence shell of a transition-metal center, and are induced by covalently σ - and π -bonded ligands. They are an integral part of the bonds formed using metal orbitals possessing d-character. It is then the different nodal structures of p and d wavefunctions that give rise to different atomic polarization patterns at main group metals and transition metals. Our study thus validates the earlier suggestion made by Szentpály and Schwerdtfeger,^[63] that polarization of a metal center and simultaneous d-orbital contribution are not different but rather two sides of the same coin, since it is the subvalence ($n-1$)d orbitals that are responsible for the polarization of the metal core.

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