DFT Calculations of ^{99}Ru Chemical Shifts with All-Electron and Effective Core Potential Basis Sets

Alessandro Bagno*[a] and Marcella Bonchio[a]

Keywords: Density functional calculations / Effective core potentials / NMR spectroscopy / Ruthenium

The nuclear shielding of ^{99}Ru in several complexes has been investigated computationally by DFT methods with effective core potential and all-electron basis sets. Shieldings calculated with ECP bases correlate very satisfactorily with available experimental data, although they are ca. one order of magnitude lower than the experimental values. The influence of molecular geometry (semiempirical vs. DFT) on the nuclear shielding is also examined and discussed, particularly in the case of species containing Ru–S bonds {[RuCl$_2$(DMSO)$_4$] and α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$}. It is shown that such calculations may help the assignment of signals in ^{99}Ru NMR spectra of mono- and polynuclear complexes.

Introduction

NMR spectroscopy of transition metal nuclei is a very attractive tool for the elucidation of the structures of complexes of transition metals, and also for the determination of structure-activity relationships, since it directly probes the atomic centre most often responsible for reactivity, e.g. in catalysis.[1] However, general application of this experimental tool is often plagued by difficulties. Most transition metal nuclei span a very wide chemical shift range (10^3-10^4 ppm), and the dependence of this on the multiple coordination and binding modes of these metals is not easily predictable.[2,3] Furthermore, the majority of such nuclei have $I >$ 1/2 and, as a result, NMR spectral lines tend to be broad, except where the local symmetry around the metal atom is relatively high. The practical difficulties associated with the detection of broad lines, together with the wide chemical shift range, sometimes renders signal assignment or even detection problematic. Therefore, it is highly desirable to be able to predict the major features of these NMR spectra.

Quantum chemical methods have proved very effective in predicting the nuclear shielding of many nuclei,[4] including transition metals.[5−7] Density-functional theory has proved to be especially effective in this regard.[5−8] However, such calculations with conventional all-electron basis sets on 2nd-row (and especially 3rd-row) transition metals are hampered by the rapid increase in the computational cost when many such heavy atoms are present (which is an important area of application; see below), and also by the onset of relativistic effects.[9] The obvious solution to this problem would be to employ a basis set with effective core potentials (ECPs), where the core electrons up to a given shell are treated in a simplified way by means of pseudopotentials (which also incorporate some relativistic corrections). The difficulty with regard to the calculation of NMR properties is that the functional form of ECPs leads, by construction, to incorrect behaviour (tending asymptotically to zero) at the nucleus. As a result, nuclear shieldings will be substantially underestimated.[10]

In relation to this issue, Moore and Healy[11] analysed the dependence of titanium shielding in titanium tetrahalides on all-electron and ECP basis sets. They found that the shielding contribution from inner shells is large but not very dependent on the basis set and the nature of the ligand, and that the contribution from the outermost core electrons (3s and 3p) is much smaller in magnitude, is paramagnetic and varies considerably. Therefore, these results suggest that the core contribution is essentially "transferable" among several species; however, the scope of such results is rather small, also considering the structural similarity of the species investigated.

Our own previous work on ^{183}W chemical shifts is consistent with the above results, which showed that the shieldings associated with a series of mono- and polynuclear tungsten complexes, calculated with ECP basis sets, are underestimated by ca. one order of magnitude. However, they correlate very well with experimental chemical shifts over a range of 8000 ppm.[12] We were then encouraged to expand the scope of these calculations to other transition metals of current interest.

Among the transition metals, ruthenium exhibits the widest range of oxidation states (eleven, from −II to +VIII) and several coordination geometries in each electronic configuration, as revealed by the large number of complexes

---

[a] Centro CNR Meccanismi Reazioni Organiche, Dipartimento di Chimica Organica, Università di Padova,
Via Marzolo 1, 35131 Padova, Italy
Fax: (internat.) + 39-049/827-5239
E-mail: alessandro.bagno@unipd.it

Supporting information for this article is available on the WWW under http://www.eurjic.com or from the author.

known that are of considerable interest in catalysis.[13] Ruthenium catalysts have indeed proved to be effective in a wide variety of organic transformations, generally featuring high efficiency and selectivity. These reactions include some fundamental processes, i.e. hydrogenation, carbon−carbon bond formation, and oxygenation by dioxygen activation.[13] In the latter field, two fairly diverse ruthenium-based catalysts, one carrying the tetramesitylporphyrinato ligand[14] and the more recent one using a totally inorganic polyoxotungstate framework,[15] have been claimed to be the most promising dioxygenase mimicking systems.

Ruthenium possesses two magnetically active isotopes (^{99}Ru and ^{101}Ru), both having $I > 1/2$, and hence are quadrupolar.[2,3] However, NMR spectroscopic investigations are usually restricted to ^{99}Ru ($I = 5/2$, $Q = 7.9$ fm^2),[16] since the other nuclide has a larger Q value. Even so, the NMR sensitivity of ^{99}Ru is rather low, which is often further complicated by the broad lines that are observed in species of low symmetry. It should also be mentioned that ruthenium NMR spectroscopy is practically feasible only on diamagnetic complexes, Ru^{II} (d^6) and Ru^{VIII} (d^0) species.

A relatively small data base of experimental NMR chemical shifts is available,[17−21] since the experimental difficulties mentioned above have prevented the detection of such signals in several low-symmetry environments.[2,3] However, the scope of ^{99}Ru NMR spectroscopy can indeed be broadened with modern spectrometers, as recently shown by Elsevier and co-workers;[22] further improvements regarding low-symmetry complexes are obtained by using supercritical fluids as solvents, where rotational correlation times can be decreased to a useful extent.[23] However, the available data extends over a few major types of compounds, notably various substituted bipyridyl, pyrazinyl, and mixed derivatives. ^{99}Ru shielding is extremely sensitive to its environment, spanning a known range of over 10^4 ppm from $\delta = -1363$ for Ru(cp)$_2$ to $\delta = 16050$ for Ru(H$_2$O)$_6^{2+}$.

Only one major computational study of ^{99}Ru NMR spectroscopic properties is available.[24] This work focussed on the quantitative prediction of such chemical shifts in a series of Ru complexes (mostly sharing a similar ligand pattern), which strictly mandates the use of all-electron basis sets. Thus, a comprehensive investigation of the performance of various basis sets and density functional methods was undertaken, which showed the high degree of accuracy that can be attained in such calculations. In particular, the better performance of hybrid functionals such as B3LYP was noted, both in terms of geometry and NMR spectroscopic properties.

However, as mentioned above, calculations with all-electron basis sets are intractable for large systems. Hence, in connection with the general interest in the catalytic properties of ruthenium-substituted polyoxometalates,[15,25,26] and based on our previous results[12] for ^{183}W, we have compared the performance of all-electron and ECP basis sets. We have carried out a computational investigation of the NMR spectroscopic properties of some ruthenium complexes for which experimental spectra, spanning most of the known shift range, are available. Our analysis includes a ruthenium-substituted polyoxotungstate anion, whose structural features and nuclear magnetic properties will be discussed in terms of the correlation with the ^{99}Ru NMR results.[26]

Computational Details

Few all-electron Gaussian basis sets are available for Ru;[27−30] in this study we employed the double-zeta polarised DZVP basis set.[29,31] No relativistic corrections were made, since very good results have also been obtained with non-relativistic calculations.[24] Since our earlier work on ^{183}W showed a similar performance of several ECPs,[12] notably those by Hay and Wadt (LANL2DZ),[32] Stevens−Basch−Krauss (CEP-121G)[33] and Dolg et al. (SDD),[34] this study will be limited to the first two.

In some cases (see Results) the LANL2DZ basis was augmented with one or two d functions from the 6-311G(d,p) or 6-311G(2d,2p) basis sets,[31] as follows. S: $\zeta = 0.650$ or $\zeta = 1.300, 0.325$; Cl: $\zeta = 1.500, 0.375$; C: $\zeta = 0.313$ or $\zeta = 1.252, 0.313$. Basis-set augmentation is denoted as LANL(nd,nd), where the first item refers to n d functions on S atoms, and the second (if present) to n d functions on Cl atoms. Thus, the basis augmented with 2 d functions both at S and at Cl will be denoted as LANL(2d,2d). The use of such augmented basis sets for the calculation of chemical shifts requires a corresponding augmentation of the basis set of the commonly accepted reference compound Ru(CN)$_6^{4-}$,[2,3] for which LANL(2d) and LANL(2d,2d) are identical since the augmentation always refers to carbon atoms. Hence, the LANL(2d) basis for Ru(CN)$_6^{4-}$ is equivalent to LANL(2d,2d) for S and Cl, since the basis of all ligands is augmented.[35] However, the augmentation of LANL(d) for Ru(CN)$_6^{4-}$ cannot be made in a consistent way, because this would actually imply one extra d function on just two equatorial carbon atoms, i.e. an inconsistent modelling of the cyano ligands. Hence, in this case only the shieldings calculated with this basis (but not the chemical shifts) will be compared.

^{99}Ru shieldings were calculated with the GIAO method by means of density functional theory (Becke's hybrid 3-parameter functional with Lee−Yang−Parr correlation, B3LYP[36])[24] and a (99,302) integration grid. Only the isotropic part of the shielding tensor [$\sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$] is given. Calculated chemical shifts ($\delta = \sigma_{\text{ref}} - \sigma$) are referred to Ru(CN)$_6^{4-}$. All calculations were carried out with GAUSSIAN 98.[37]

Results and Discussion

For our analysis we chose a number of species of moderate size, evenly spanning the entire known chemical shift range (Table 1). In addition to these complexes, we also investigated a polyoxotungstoruthenate, α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$, which can be obtained by metallation of the

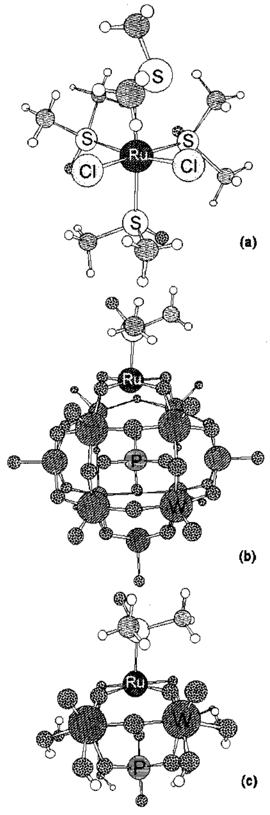
Table 1. Calculated energies (au), calculated and experimental NMR chemical shifts (ppm) of ^{99}Ru in ruthenium complexes with the LANL2DZ and CEP-121G ECP basis sets

Species	LANL2DZ						CEP-121G			
	PM3(tm)[a]			LANL2DZ[b]			CEP-121G[c]			Exptl.
	E	σ	calcd. δ[d]	E	σ	calcd. δ[d]	E	σ	calcd. δ[d]	δ[e]
$Ru(cp)_2$[f]	−480.888559	−183.1	−88	−480.905987	−396.0	−133	−156.404137	−343.7	−235	−1270,[18] −1363[g]
$Ru(CN)_6^{4-}$	−650.513909	−271.3[h]	0	−650.538156	−529.0[i]	0	−186.758568	−579.2[j]	0	0[17,18]
$[Ru(CO)_3Cl_3]^-$ [k]	−478.920626	−317.8	46.5	−478.947778	−477.8	−51.3	−203.779083	−484.1	−95.1	816[24]
RuO_4	−394.634978	−671.0	400	−394.638460	−731.2	202	−157.681749	−763.7	184	2021[18]
$Ru(bpy)_3^{2+}$	−1579.493860	−838.1	567	−1579.514435	−998.0	469				4518,[18] 4609[19]
$Ru(NH_3)_6^{2+}$	−432.801885	−838.0	567	−432.837757	−1542	1013	−163.795650	−1688	1109	7680,[17] 7821[18]
$Ru(H_2O)_6^{2+}$	−551.890651	−2055	1784	−551.956823	−2741	2212	−196.478459	−3019	2440	16050[20]
$[RuCl_2(DMSO)_4]$[l]	−784.029546	−1039	768	−784.133356	−1650	1121	−287.549287	−1816	1237	3976[26]

[a] B3LYP/LANL2DZ//PM3(tm). [b] B3LYP/LANL2DZ//B3LYP/LANL2DZ. [c] B3LYP/CEP-121G//B3LYP/CEP-121G. [d] $\delta = \sigma_{ref} - \sigma$, relative to $Ru(CN)_6^{4-}$. [e] Literature reference given as superscript. [f] Eclipsed rings as in the experimental structure. The corresponding structure with staggered rings has the same energy, and $\sigma = -183.6$ [PM3(tm) geometry] or $\sigma = -405.6$ (LANL2DZ geometry). [g] Redetermined in this work (CH_2Cl_2 solution, 25 °C; see ref.[26] for experimental details). [h] Ru−C = 1.986 Å. [i] Ru−C = 2.105 Å. [j] Ru−C = 2.130 Å. [k] *fac* isomer. [l] *cis,fac* isomer (Scheme 1).

lacunary α-Keggin polyoxotungstate α-$[PW_{11}O_{39}]^{7-}$ with $[RuCl_2(DMSO)_4]$ under microwave irradiation.[26] The ^{99}Ru signal of α-$[PW_{11}RuO_{39}(DMSO)]^{5-}$ (observed at $\delta = 7737$), is quite removed from that of the ruthenium precursor ($\delta = 3976$), and provides the first NMR spectrum of ruthenium embedded in a polyoxotungstate cage.[26] Therefore, it is of interest to extend the scope of our study to Ru complexes in this new environment.

Geometrical features are discussed only in relevant cases (Scheme 1);[38−41] all calculated structures are given as Supporting Information as PDB files.



Scheme 1. Calculated structures of ruthenium complexes. (a) $[RuCl_2(DMSO)_4]$ (B3LYP/DZVP); (b) α-$[PW_{11}RuO_{39}(DMSO)]^{5-}$ [PM3(tm)]; (c) the model fragment $[PW_4RuO_{10}(OH)_8(DMSO)]^{5-}$ [B3LYP/LANL(d); see text]; O dotted, C solid grey, H white

Shielding Calculations with ECP Basis Sets

The size of most complexes investigated in this work lies within the scope of current ab initio or DFT geometry optimisations. However, a comparison with shieldings obtained at geometries optimized with the PM3(tm) semiempirical level[43] was deemed necessary in order to establish whether shieldings calculated with the latter simpler method have some predictive value for ruthenium-containing polyoxometalates, whose size would be extremely demanding for higher-level methods.

Thus, ^{99}Ru shieldings were obtained for a series of Ru complexes, whose structures were optimised as reported in Table 1. The results calculated with ECP basis sets are presented in Table 1 and Figure 1.

Inspection of Table 1 firstly shows that with ECP basis sets the values of σ are smaller than the experimental values by one order of magnitude. However, calculated δ values correlate very well with the experimental data, as can be seen from the graphs in Figure 1. A linear fit is seen for δ_{calcd} vs. δ_{exptl} ($\delta_{calcd} = a\delta_{exptl} + b$). PM3(tm) geometry: $a = 0.10\pm0.04$, $b = 69\pm85$, $r^2 = 0.96$; LANL2DZ geometry: $a = 0.139\pm0.006$, $b = -59\pm42$, $r^2 = 0.995$; CEP-121G geometry: $a = 0.156\pm0.006$, $b = -90\pm45$, $r^2 = 0.997$. These correlation parameters can be used to estimate "experimental" chemical shifts from $\delta_{exptl} = (\delta_{calcd} - b)/a$. Based on the above standard deviations of a and b, error propagation formulas yield standard deviations on the estimated δ_{exptl} of about 300 ppm. This is of the same order as the typical spread of experimental values, which often differ by 200−300 ppm [up to 3000 ppm for $Ru(H_2O)_6^{2+}$].

Despite the low slope values observed (see below), the good correlations show that the calculation with ECP basis sets only introduces a systematic error, which is remarkably

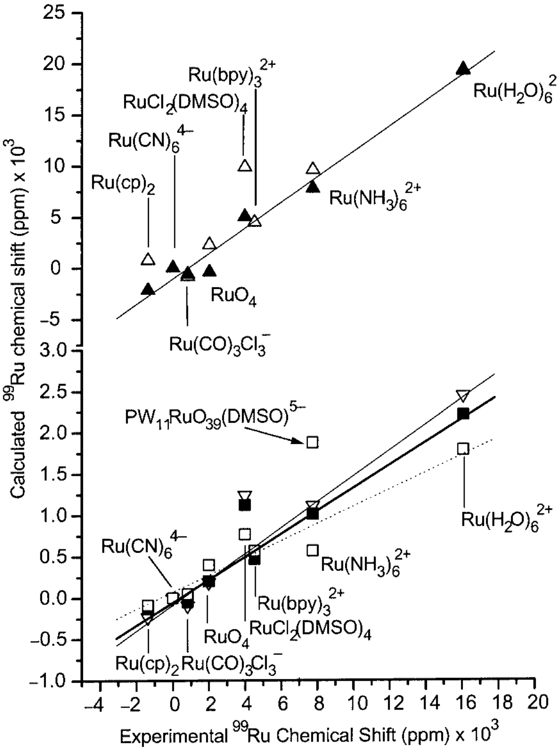


Figure 1. Correlation between experimental and calculated ^{99}Ru shieldings with ECP or all-electron basis sets; results of linear fittings are reported as $\delta_{calcd} = a\delta_{exptl} + b$; bottom panel: (a) empty squares, dotted line: B3LYP/LANL2DZ//PM3(tm); $a = 0.10 \pm 0.04$, $b = 69 \pm 85$, $r^2 = 0.96$; fit does not include the data for [RuCl$_2$(DMSO)$_4$] and α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$; (b) solid squares, solid thick line: B3LYP/LANL2DZ//B3LYP/LANL2DZ; $a = 0.139 \pm 0.006$, $b = -59 \pm 42$, $r^2 = 0.995$; (c) down triangles, solid thin line: B3LYP/CEP-121G//B3LYP/CEP-121G; $a = 0.156 \pm 0.006$, $b = -90 \pm 45$, $r^2 = 0.997$); fits do not include the data points for [RuCl$_2$(DMSO)$_4$]; top panel: (d) empty triangles, no fit line: B3LYP/DZVP//B3LYP/LANL2DZ; (e) solid triangles, solid line: B3LYP/DZVP//B3LYP/DZVP; $a = 1.24 \pm 0.08$, $b = -1060 \pm 570$, $r^2 = 0.989$

constant for a wide array of species. The above correlations hold through the known chemical shift range of ca. 20000 ppm, thereby broadening the scope of such calculations beyond the range examined, e.g., in ref.[24]

Test calculations with pure functionals (BLYP, PW91PW91; data not reported) yielded very similar results in terms of absolute shieldings and more so in terms of the slope of the correlation lines.

We would like to point out that anionic, neutral and cationic species are equally well modelled, which implies a relatively minor solvent effect in determining the ^{99}Ru chemical shift. This may simply be a consequence of the very large range of chemical shifts investigated (i.e., solvent effects are smaller than our estimated accuracy of ±300 ppm), and should call for caution whenever smaller ranges are investigated, or when complexes with a labile coordination sphere are considered.

We also note that the performance of LANL2DZ and CEP-121G (at the respective geometries) is quite similar (Figure 1), but differ with the results of ref.[11] for Ti. The comparison of shifts calculated with a DFT geometry, rather than a semiempirical geometry shows that the fit quality is generally better even though the slope of the correlation line is not very different.

Hence, despite this large systematic error, ECP shielding calculations effectively model ^{99}Ru shifts to an accuracy that will enable the experimental NMR spectroscopist to close in on the spectral region where the signals may be expected, with obvious practical advantages. However, there are three major discrepancies emerging from the correlation in Figure 1.

(a) The calculated shielding of [Ru(NH$_3$)$_6^{2+}$], using the PM3(tm) geometry, fits rather badly in the correlation line, whereas if the geometry is optimized by an ECP method, the data fits very well; (b) the shielding of [RuCl$_2$(DMSO)$_4$] is only fairly well modelled with the PM3(tm) geometry, whereas both ECP geometries lead to an unacceptably deshielded chemical shift; (c) the shielding of α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$ is grossly overestimated at the PM3(tm) geometry (the only practical approach for a molecule of this size), which yielded a Ru−S distance of 2.276 Å (Scheme 1). In the latter two cases, we are dealing with species possessing Ru−S bonds. The nature of the bonding of DMSO to ruthenium is a matter of current interest, justified by the recent discovery that haloruthenium (sulfoxide) complexes exhibit a remarkable anti-tumour activity, in addition to being versatile oxidation catalysts.[44] The effect of the Ru−S bond length on the ^{99}Ru shielding in [RuCl$_2$(DMSO)$_4$] and α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$ has been studied in detail (see below).

Shielding Calculations with the All-Electron DZVP Basis Set

Although in practical terms ECP basis sets seem to perform remarkably well (except for the large systematic error), it is worthwhile to compare such results with the performance of an all-electron basis set, where the contribution of core electrons is explicitly taken into account. Thus, ^{99}Ru shieldings have been calculated for the same data set seen before, using both the previous LANL2DZ and newly optimized DZVP geometries (Table 2 and Figure 1).

The first major difference with respect to the previous results is, of course, that the order of magnitude of calculated shifts is now correct, as shown by the correlation parameters ($a = 1.24 \pm 0.08$, $b = -1060 \pm 570$, $r^2 = 0.989$), with a slope now close to unity. Shieldings calculated at this level of theory are, in fact, overestimated by 20%, which shows the need for a better basis set in order to arrive at the desired unit slope.[24] However, this is sufficient for the purposes of this work, since a well-behaved general trend is apparent.

The much better performance of the DZVP than the LANL2DZ geometries is also apparent. Since *valence* electrons are treated on a similar footing by both basis sets (e.g., no relativistic corrections are made, while scalar relativistic corrections are present only in the pseudopotentials pertaining to core electrons in LANL2DZ), the worse performance of the latter basis seems due to a deficiency in the valence region. In fact, the species giving the worst fitting (Figure 1d) is [RuCl$_2$(DMSO)$_4$], for which the LANL2DZ

Table 2. Calculated energies [au], calculated and experimental chemical shift [ppm] of ^{99}Ru in ruthenium complexes with the DZVP basis set

Species	LANL2DZ[a]			DZVP[b]			Exptl.
	E	σ	δ[c]	*E*	σ	δ[c]	δ[d]
$Ru(cp)_2$[e]	−4830.422148	−772.6	757	−4830.424271	−370.8	−2151	−1270, −1363
$Ru(CN)_6^{4-}$	−5000.087074	−15.70	0	−5000.124589	−2522[f]	0	0
$[Ru(CO)_3Cl_3]^-$	−6164.101958	−1682	−840	−6164.106358	−1920	−602	816
RuO_4	−4744.076322	−2299	2283	−4744.077196	−2111	−411	2021
$[RuCl_2(DMSO)_4]$[g]	−7576.467389	−9851	9835	−7576.547516	−7526	5004	3976
$Ru(bpy)_3^{2+}$	−4830.422148	−4463[h]	4447	[i]			4518, 4609
$Ru(NH_3)_6^{2+}$	−4782.293995	−9558	9542	−4782.298573	−10254	7731	7821, 7680
$Ru(H_2O)_6^{2+}$	−4901.402267	−19195	19179	−4901.405323	−21789	19267	16050

[a] B3LYP/DZVP//B3LYP/LANL2DZ, except where indicated. [b] B3LYP/DZVP//B3LYP/DZVP. [c] $\delta = \sigma_{ref} - \sigma$, relative to $Ru(CN)_6^{4-}$. [d] See Table 1 for sources. [e] See footnote [f] to Table 1. [f] Ru−C = 2.145 Å. [g] See footnote [l] to Table 1. [h] PM3(tm) geometry. [i] Not calculated, because the chemical shift lies well within the range encompassed by the other species and this compound is well behaved at the other theoretical levels, so that this large calculation is not expected to reveal new trends.

basis shown below is seen to be inadequate to model the Ru−S and Ru−Cl bonds.

Hence, in general terms the DZVP basis set has a performance similar to that of the ECP bases seen before. However, there is a considerable time penalty involved, DZVP calculations taking ca. 4 times longer than the corresponding LANL2DZ ones. The time issue may become crucial when planning to investigate systems containing a large number of heavy atoms, like polyoxometalates (see below).

Comparison of Shieldings Calculated with All-Electron and ECP Basis Sets

The large underestimation of the shieldings calculated with an ECP basis set is a known effect, previously observed by Ridard et al.[10] for ^{31}P, and by ourselves[12] for ^{183}W. This underestimation arises because molecular orbitals built from ECPs fall asymptotically to zero at distances smaller than the core radius, thereby losing all nodal features of orbitals replaced by the ECP. Since the shielding constant is calculated from integrals containing an r_N^{-3} term (r_N being an electron−nucleus distance), these integrals become too small in the vicinity of the nucleus.[10,12] The relationship between the data obtained by all-electron (AE, with DZVP) or ECP (with LANL2DZ) calculations is further investigated by dissecting the σ values into its diamagnetic (σ_d) and paramagnetic (σ_p) components, for a few representative complexes (Table 3).

Table 3. Diamagnetic and paramagnetic contributions to ^{99}Ru shielding with the DZVP and LANL2DZ basis sets

	DZVP[a]		LANL2DZ[a]	
	σ_d	σ_p	σ_d	σ_p
$Ru(cp)_2$	4281	−4652	252.4	−648.3
$Ru(CN)_6^{4-}$	4265	−6787	243.1	−772.2
$Ru(NH_3)_6^{2+}$	4263	−14520	234.6	−1776
$Ru(H_2O)_6^{2+}$	4261	−26050	234.2	−2975
RuO_4	4260	−6370	233.1	−964.4
av.	4266±10		239±10	

[a] At the respective geometries; see Tables 1−2.

Table 3 shows that σ_d is remarkably constant for all species investigated, with an average value of 4260±10 ppm (AE) or 240±10 ppm (ECP). The definition of core electrons in the LANL2DZ basis set includes all electrons up to the 3d shell. The hypothetical Ru^{16+} ion has only core electrons; accordingly, no shielding is calculated with the ECP basis, whereas σ_d = 3993 ppm is calculated with DZVP, which is in reasonably good agreement with the average value given above. On the other hand, the Ru^{8+} ion (with a [core] $4s^24p^6$ configuration) yields quite similar σ_d values with both AE and ECP methods (176 and 144 ppm, respectively). The further contribution to σ_d from 4d electrons is highlighted by the values for Ru^{2+} ([core] $4s^24p^64d^6$), which is again quite similar in both cases (80 ppm). Hence, although the valence region of the LANL2DZ basis is of somewhat lower quality than that of DZVP, the contribution of valence electrons to σ_d is calculated to be very similar; the small sensitivity of σ_d to the basis set is further confirmed. Indeed, the large difference of ca. 4000 ppm arising from the core electrons (being just an additive term) is irrelevant in the calculation of chemical shifts.

With regard to σ_p, we note that only a contribution from the 4d electrons can be expected, since all lower shells are closed. Thus, for Ru^{2+} we calculate σ_p = 362000 and 74000 ppm in the AE and ECP bases, respectively, with a ratio of 4.9. Table 3 shows that for Ru complexes a similar relationship also holds, $\sigma_p^{AE}/\sigma_p^{ECP} = 7-9$. A linear fitting of σ_p^{AE} vs. σ_p^{ECP} yields a slope of 9.1, which corresponds to the relative slope (8.9) of the correlation lines in Figure 1b and e, and confirms that the large difference between experimental and ECP-calculated chemical shifts arises entirely from the paramagnetic term, in turn arising essentially from 4d electrons.

Ruthenium Shielding in $RuCl_2(DMSO)_4$

As noted above (see Figure 1), the calculated shifts for $RuCl_2(DMSO)_4$ fit reasonably well with the correlation line from the data obtained using the DZVP geometry, whereas all those with ECP or PM3(tm) geometries are too deshielded. We have investigated the origin of this discrepancy in

Table 4. Calculated and experimental Ru−S distances [Å] of the coordinated sulfur atoms in $[RuCl_2(DMSO)_4]$

Geometry[a]	Ru−S eq	 eq	 ax	Ru−Cl		Av. diff.[b]
PM3(tm)	2.350	2.348	2.323	2.351	2.371	0.068
LANL2DZ	2.480	2.480	2.470	2.481	2.486	0.150
LANL(d)	2.376	2.369	2.346	2.515	2.521	0.096
LANL(2d)	2.345	2.336	2.310	2.530	2.539	0.082
LANL(2d,2d)	2.356	2.347	2.308	2.474	2.480	0.063
CEP-121G	2.490	2.492	2.478	2.486	2.490	0.158
DZVP	2.397	2.400	2.352	2.474	2.480	0.091
Experimental[c]	2.274	2.284	2.245	2.421	2.424	−

[a] B3LYP calculations, except PM3(tm). [b] Average of absolute deviations over all bonds for the specified level (see text). [c] Ref.[41]

detail by analysing the effect of augmenting the ECP basis on (a) the geometry (especially the Ru−S bonds) and, (b) the ^{99}Ru shielding. The experimental and calculated Ru−S distances are reported in Table 4, whereas basis set and geometry effects on the calculated shielding are collected in Table 5.

In the X-ray structure,[41] Ru−S distances of the three *S*-coordinated DMSO molecules are 2.274, 2.284 Å (equatorial) and 2.245 Å (axial). In the PM3(tm) structure, relative Ru−S distances (Table 4) agree with the experimental ones, but the PM3(tm) method overestimates the Ru−S distances by 0.07 Å on average. Geometry optimization with both the LANL2DZ and CEP-121G basis sets yield very similar Ru−S distances (Table 4). However, although the relative distances are once again correct, these basis sets overestimate experimental Ru−S distances by 0.21−0.22 Å, with a poor fit with either correlation already mentioned.

A possible cause for this poor performance may lie in an inadequate treatment of the valence region of the S or Cl atoms. To address this issue, the LANL2DZ basis was augmented at the sulfur and/or chlorine atoms [LANL(d), LANL(2d), and LANL(2d,2d); see Computational Details].

Table 4 shows that geometry optimisation with the LANL(d) and LANL(2d) basis sets leads to a marked shortening of the Ru−S distances. However, they remain longer than the experimental distances (by 0.10 and 0.06 Å, respectively), while the Ru−Cl bond lengths are substantially overestimated (by ca. 0.1 Å). Augmentation of the chlorine basis [LANL(2d,2d)] also results in a slight lengthening of the Ru−S bonds and a shortening of the Ru−Cl bonds, which deviate by 0.05−0.06 Å from the experimental values. The latter basis is the best, as indicated by the average deviation of 0.063 Å over the Ru−S and Ru−Cl bonds (Table 4).

Shielding calculations were performed with all variants of the LANL2DZ basis, in combination with geometries obtained at the various levels available, as detailed in Table 5. We would like to mention at this point that no calculation was carried out at the experimental geometry, to ensure consistency of treatment with the other species.

The effect of the geometry and basis set on the calculated shielding can be summarized as follows. Augmenting the LANL2DZ basis set with polarisation functions on the ligands, i.e. improving their valence region, has remarkable effects on the geometry, as seen before. Thus, σ values calculated with the augmented basis sets (between −1296 and −1059) are substantially more shielded than the reference value of −1650 (Table 1), which goes in the right direction. However, this effect is primarily a result of the mentioned geometry changes, rather than of the basis set per se. For example, shieldings of −1650, −1296, or −1211 are calculated with the same basis set (LANL2DZ) at the LANL2DZ, LANL(d), or LANL(2d) geometry, respectively. Conversely, the shielding calculated with the LANL(2d) basis at the LANL2DZ geometry (−1521) is only slightly better than the reference value.

Further improvement is achieved by adopting the augmented basis for the shielding calculation also, which brings the value down to −1089 with LANL(2d). Augmentation of the Cl basis, once again, has a noticeable effect on the shielding (−1059), only when the calculation is run on the optimized structure. The results of these calculations are

Table 5. Calculated and experimental NMR chemical shifts [ppm] of ^{99}Ru in $Ru(CN)_6^{4-}$ and $RuCl_2(DMSO)_4$ with the LANL2DZ ECP basis set, augmented variously

Level[a]	$Ru(CN)_6^{4-}$ σ_{ref}	$[RuCl_2(DMSO)_4]$ σ	 calcd. δ[b]
LANL//LANL	−529.1	−1650	1121
LANL//LANL(d)	−565.3	−1296	[c]
LANL(d)//LANL(d)	−533.2	−1171	[c]
LANL//LANL(2d)[d]	−479.8	−1211	731.2
LANL(2d)//LANL	−509.7	−1521	1011
LANL(2d)//LANL(2d)	−479.8	−1089	609.2
LANL(2d,2d)//LANL(2d)	−479.8	−1087	607.2
LANL(2d,2d)//LANL(2d,2d)	−479.8	−1059	579.2
LANL(2d,2d)//PM3(tm)	−258.2	−930.7	672.5

[a] All calculation with the B3LYP functional; see Table 1 for general remarks and experimental values. The LANL2DZ basis is abbreviated as LANL. Basis-set augmentation is denoted as LANL(nd,nd), where the first item refers to *n* d-functions on sulfur atoms, and the second (if present) to *n* d-functions on chlorine atoms (see Computational Details). For $Ru(CN)_6^{4-}$, LANL(2d) and LANL(2d,2d) are identical since the augmentation always refers to carbon atoms. [b] $\delta = \sigma_{ref} - \sigma$; the calculation for $Ru(CN)_6^{4-}$ is carried out at the corresponding level. [c] σ_{ref} cannot be consistently calculated (see Computational Details). [d] Ru−C = 2.096 Å.

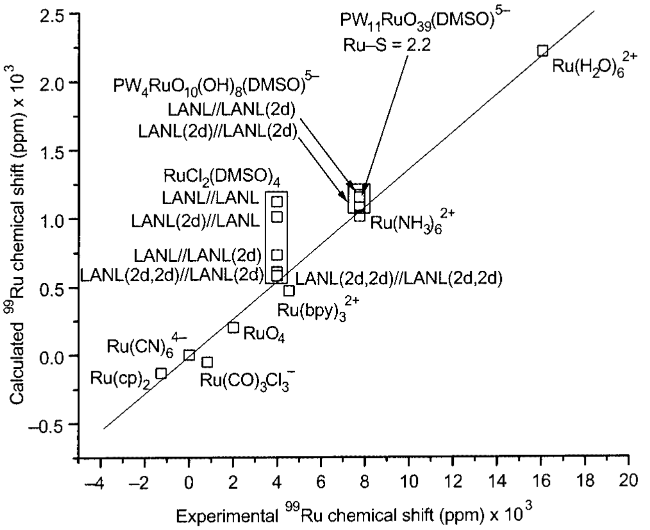


Figure 2. Basis-set and geometry effects on ^{99}Ru shieldings of [RuCl$_2$(DMSO)$_4$], [PW$_4$RuO$_{10}$(OH)$_8$(DMSO)]$^{5-}$, and α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$ (not included in the fit; see text for these data); the geometry is at the B3LYP/LANL2DZ level (cf. Figure 1), except where noted; the LANL2DZ basis is abbreviated as LANL

summarized in Figure 2, which highlights the progressive trend of the calculated values towards a good fit with the correlation line. The value $\delta = 4590$ is obtained after the calculated δ value of 579 is corrected by the appropriate fitting parameters, and compares with the experimental value ($\delta = 3976$).

At the PM3(tm) geometry, shieldings of −1039 (Table 1) and −931 (Table 5) are calculated with LANL2DZ and LANL(2d,2d), respectively. This point further illustrates the dependence of the shielding on geometry, and highlights the better performance of augmented LANL2DZ.

A similar effect was found in the case of [Ru(CO)$_3$Cl$_3$]$^-$. Again, a geometry optimisation with the LANL(2d,2d) basis leads to a better modelling of the experimental structure, with an average deviation of the Ru−C and Ru−Cl bond lengths from those of the experimental structure[24] of 0.04 Å (0.06 Å with LANL2DZ). Accordingly, a slight improvement is noted in the calculated chemical shift ($\delta = -17$, rather than $\delta = -51$ with the non-augmented basis) which has a better fit in the correlation line, with an experimental value of $\delta = 816$.

These results allow us to draw the following conclusions. (a) Although augmenting the ECP basis set with polarisation functions on the ligands has remarkable effects on the molecular geometry, any effect on the ruthenium shielding is mostly due to such geometry changes, since calculations with augmented basis sets but with non-optimised geometries only lead to minor improvements. (b) Calculated chemical shifts correlate with experimental values over the whole chemical shift range, even though some deviations from experimental geometries may be present, at least in the case of [RuCl$_2$(DMSO)$_4$]. (c) Chemical shifts calculated with various augmented valence regions converge to a value falling within the correlation line previously found; this confirms that the large scaling factors do not depend much on the chemical nature of the complex. However, the adequacy of such scaling factors in obtaining very accurate estimates is, perhaps, yet to be assessed.

Ruthenium Shielding in α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$

Although an experimental X-ray structure is not available, the general structural features are known from ^{183}W, ^{31}P, and ^{1}H NMR spectroscopic data.[26] The data point out that the complex (a) retains the basic α-Keggin structure, with one Ru atom replacing one W atom, and (b) one DMSO molecule is coordinated to the Ru atom, presumably through the S atom rather than the O atom. This indication is further strengthened by the fact that the PM3(tm) geometry optimisation of a structure with an *O*-coordinated DMSO molecule leads to the *S*-coordinated molecule.

The large size of this species renders a PM3(tm) geometry optimisation as the only feasible approach, which yields an Ru−S distance of 2.276 Å (structure b in Scheme 1). We note that this distance is shorter than the shortest distance in RuCl$_2$(DMSO)$_4$ (2.323 Å) computed at the same level. The calculated shielding at the B3LYP/LANL2DZ level is $\sigma = -2146$, corresponding to a calculated value of $\delta = 1875$; after conversion into an estimated δ value through the pertinent correlation parameters, this corresponds to a very large overestimation ($\delta = 19000$ vs. the experimental value of $\delta = 7737$). The strategy adopted for improving the predictive power of such calculations is described as follows (see Table 6).

Table 6. Geometry effects on the ruthenium shielding in polyoxotungstoruthenates[a]

Geometry	*r*(Ru−S) [Å]	*E* [au]	σ
α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$			
PM3(tm)	2.276[b]	−3947.416803	−2146[c]
PM3(tm)	2.245[d]	−3947.412974	−1916[c]
PM3(tm)	2.200[d]	−3947.410692	−1681[e]
[PW$_4$RuO$_{10}$(OH)$_8$(DMSO)]$^{5-}$			
LANL2DZ	2.849[b][f]	−2196.998676	−3187
LANL2DZ	1.990[d][g]	−2196.852029	−1651
LANL(2d)	2.196[b]	−2197.144188	−1620[h]
LANL(2d)	2.196[b]	−2197.015405	−1697[i]

[a] B3LYP/LANL2DZ, except where noted. [b] Optimised Ru−S distance. [c] SCF convergence criteria reduced to 10^{-7}. [d] Ru−S distance constrained as stated. [e] SCF convergence criteria reduced to 10^{-6}. [f] Partially optimised structure (expulsion of DMSO). [g] Rest of molecule as in the preceding item. [h] Shielding calculated with the LANL(2d) basis set. [i] Shielding calculated with the LANL2DZ basis set.

The Ru−S distance was firstly constrained to 2.245 Å, as in the experimental structure of [RuCl$_2$(DMSO)$_4$] (Table 4) and reoptimised by PM3(tm) under this constraint. A smaller value of σ (−1916) was obtained (Table 6), which corresponds to $\delta = 15900$; however, this is still too high. Nevertheless, this result provides a first indication that a relatively short Ru−S distance should be expected.

In view of the huge computational cost of calculations on the whole complex, test calculations were run on the model fragment $[PW_4RuO_{10}(OH)_8(DMSO)]^{5-}$, featuring only the upper lacunary sites and with some protonated WO_6 units, so as to have the same charge as the target compound (Scheme 1, structure c). A B3LYP/LANL2DZ geometry optimisation led to the expulsion of the DMSO molecule (Ru−S distance > 4 Å), and (quite predictably) to an even larger deshielding ($\sigma = -3187$).[45]

The better performance observed with the LANL(2d) basis in the case of $[RuCl_2(DMSO)_4]$ indeed suggests its use as a possible remedy. On the other hand, by constraining the Ru−S bond length to 1.990 Å, the resulting more shielded $\sigma = -1651$ value further indicates a short Ru−S bond in the species under examination.

A B3LYP/LANL(2d) geometry optimisation led to a Ru−S distance of 2.196 Å. The shielding calculated with the same basis (−1620) gives an excellent fit in the pertinent correlation line (Figure 2). The same calculation run with the non-augmented basis [i.e., LANL2DZ//LANL(2d)] yields a similar but slightly worse shielding ($\sigma = -1697$). Hence, all data point to a substantially shorter Ru−S distance in the polyoxometalate than in $RuCl_2(DMSO)_4$.

Based on these arguments, we ran a further calculation on α-$[PW_{11}RuO_{39}(DMSO)]^{5-}$ with the Ru−S distance fixed at 2.200 Å (close to the optimised value for the model, see above). The resulting shielding was $\sigma = -1681$ (Table 6). Thus, remarkably, shortening the Ru−S distance by 0.045 Å shields the ^{99}Ru nucleus by 235 ppm which, when converted into experimental data through the slope factor of 7.2, results in a value no less than 1700 ppm. This point illustrates the extreme sensitivity of ^{99}Ru chemical shifts to its coordination geometry.

Interpretation of these results should be based on the consideration that the geometry employed is derived partly (essentially all the polyoxometalate cage) from PM3(tm) and partly (the Ru−S distance) from DFT methods. However, since the Ru−S distance is apparently the most important parameter in determining the Ru shift, it is admissible to regard this data as belonging to the DFT correlation line (Figure 2), which shows an excellent fit. The calculated chemical shift would be (once corrected by the factor of 7.2) $\delta = 8700$, compared with the experimental value of $\delta = 7737$. We also note that, since the LANL(2d) basis overestimates the Ru−S distance by ca. 0.1 Å, we estimate that the distance in the polyoxometalate is 2.1 Å.

The general conclusion that can be drawn is that the valence region of the LANL2DZ basis set for sulfur is inadequate to model the Ru−S bond, leading to unacceptably long distances. However, this basis is acceptable for the calculation of the shielding, provided that the geometry is appropriate. We would also like to point out that despite the seemingly large error in this calculation (ca. 1000 ppm), this estimate would in fact be helpful in narrowing the spectral region to an extent which allows the reduction of the experimental problems associated with large spectral windows at low frequencies.[2]

Conclusion

ECP basis sets perform remarkably well in the calculation of ^{99}Ru chemical shifts, although such calculated shieldings are much smaller than those calculated by all-electron basis sets or experimental values. We should warn the reader that this approach is "semiempirical" in nature, since it assumes full transferability of the core contribution to the total shielding, and hence its cancellation when chemical shifts are calculated. We have provided a preliminary rationale for this assumption by analysing the relative contribution of the diamagnetic and paramagnetic terms; however, its scope must be independently tested, like in any other approach of this type. At this point, we have provided a set of data that should enable the NMR spectroscopist to obtain at least a rough estimate of the chemical shift of unknown complexes, even relatively large ones (after correction by an appropriate scaling factor). The all-electron DZVP basis set also performs well (albeit at an increased computational cost), particularly in the case of species containing Ru−S bonds. Such species are also successfully modelled by the LANL2DZ ECP basis set, provided that the valence region of the sulfur and chlorine atoms is augmented with d-type polarisation functions. The consistency of these data with those for ^{183}W[12] and ^{95}Mo[47] allows one to envision that the scope of such calculations can be expanded to other nuclei.

Acknowledgments

Part of this work was carried out on an SGI Origin 2000, with computer time granted by CINECA. The Authors thank Dr. A. Sartorel for his technical help.

---

[1] W. von Philipsborn, *Chem. Soc. Rev.* **1999**, *28*, 95.
[2] *Multinuclear NMR* (Ed.: J. Mason), Plenum, New York, **1987**.
[3] *Transition Metal Nuclear Magnetic Resonance* (Ed.: P. S. Pregosin), Elsevier, Amsterdam, **1991**.
[4] For a recent review, see: T. Helgaker, M. Jaszunski, K. Ruud, *Chem. Rev.* **1999**, *99*, 293.
[5] [5a] M. Bühl, O. L. Malkina, V. G. Malkin, *Helv. Chim. Acta* **1996**, *79*, 742. [5b] M. Kaupp, V. G. Malkin, O. L. Malkina, D. R. Salahub, *Chem. Eur. J.* **1996**, *2*, 24. [5c] M. Bühl, *Chem. Phys. Lett.* **1997**, *267*, 251. [5d] O. L. Malkina, B. Schimmelpfennig, M. Kaupp, B. A. Hess, P. Chandra, U. Wahlgren, V. G. Malkin, *Chem. Phys. Lett.* **1998**, *296*, 93.
[6] N. Godbout, E. Oldfield, *J. Am. Chem. Soc.* **1997**, *119*, 8065.
[7] P. J. Wilson, R. D. Amos, N. C. Handy, *Phys. Chem. Chem. Phys.* **2000**, *2*, 187.
[8] C. Adamo, V. Barone, *Chem. Phys. Lett.* **1998**, *298*, 113.
[9] See, for example: G. Schreckenbach, S. K. Wolff, T. Ziegler, *J. Phys. Chem. A* **2000**, *104*, 8244.
[10] J. Ridard, B. Levy, Ph. Millie, *Mol. Phys.* **1978**, *36*, 1025.
[11] E. A. Moore, A. Healy, *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1735.
[12] A. Bagno, M. Bonchio, *Chem. Phys. Lett.* **2000**, *317*, 123.
[13] T. Naota, H. Takaya, S. Murahashi, *Chem. Rev.* **1998**, *98*, 2599.
[14] J. T. Groves, R. Quinn, *J. Am. Chem. Soc.* **1985**, *107*, 5790.
[15] R. Neumann, M. Dahan, *J. Am. Chem. Soc.* **1998**, *120*, 11969, and references therein.
[16] *CRC Handbook of Chemistry and Physics*, 77th ed. (Ed.: D. R. Lide), CRC Press, Boca Raton, **1997**.
[17] R. W. Dykstra, A. M. Harrison, *J. Magn. Reson.* **1982**, *46*, 338.
[18] C. Brevard, P. Granger, *Inorg. Chem.* **1983**, *22*, 532.

[19] P. J. Steel, F. Lahousse, D. Lerner, C. Marzin, *Inorg. Chem.* **1983**, *22*, 1488.

[20] [20a] P. Bernhard, L. Helm, I. Rapaport, A. Ludi, A. E. Merbach, *J. Chem. Soc., Chem. Commun.* **1984**, 302. [20b] P. Bernhard, L. Helm, A. Ludi, A. E. Merbach, *J. Am. Chem. Soc.* **1985**, *107*, 312.

[21] C. Marzin, F. Budde, P. J. Steel, D. Lerner, *Nouv. J. Chim.* **1987**, *11*, 33.

[22] S. Gaemers, J. van Slageren, C. M. O'Connor, J. G. Vos, R. Hage, C. J. Elsevier, *Organometallics* **1999**, *18*, 5238.

[23] S. Gaemers, H. Luyten, J. M. Ernsting, C. J. Elsevier, *Magn. Reson. Chem.* **1999**, *37*, 25.

[24] M. Bühl, S. Gaemers, C. J. Elsevier, *Chem. Eur. J.* **2000**, *6*, 3272.

[25] C. Rong, M. T. Pope, *J. Am. Chem. Soc.* **1992**, *114*, 2932.

[26] A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, *Eur. J. Inorg. Chem.* **2000**, 17.

[27] K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.* **1987**, *8*, 880.

[28] [28a] S. Huzinaga, B. Miguel, *Chem. Phys. Lett.* **1990**, *175*, 289. [28b] S. Huzinaga, M. Klobukowski, *Chem. Phys. Lett.* **1993**, *212*, 260.

[29] N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* **1992**, *70*, 560.

[30] R. Ahlrichs, K. May, *Phys. Chem. Chem. Phys.* **2000**, *2*, 943.

[31] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, Washington 99352, USA, and funded by the U. S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U. S. Department of Energy under contract DE-AC06-76RLO1830. Contact David Feller or Karen Schuchardt for further information (see also http://www.emsl.pnl.gov:2080/forms/basisform.html).

[32] [32a] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270. [32b] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284. [32c] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[33] W. Stevens, H. Basch, J. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026.

[34] T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys.* **1996**, *105*, 1052, and previous papers by the same group.

[35] The Ru−C distance in Ru(CN)$_6^{4-}$ calculated with the LANL(2d) basis (2.096 Å) is the one that compares best with the experimental value of 2.039 Å[24] (see footnotes to Tables 1−2 for other data).

[36] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian, Inc., Pittsburgh PA, **1998**.

[38] The structure of Ru(cp)$_2$ may feature eclipsed or staggered cyclopentadiene rings, and both geometry optimizations successfully converge to the respective structures. Since the experimental structure[39] has eclipsed rings, all data presented herein will refer to structures with eclipsed rings; however, even though the calculated energy difference is negligible ($<$ 1 kcal/mol), the chemical shift difference ($<$ 100 ppm) is noticeable.

[39] [39a] G. L. Hardgrove, D. H. Templeton, *Acta Crystallogr.* **1959**, *12*, 28. [39b] P. Seiler, J. D. Dunitz, *Acta Crystallogr., Sect. B* **1980**, *36*, 2946.

[40] The X-ray structure of [RuCl$_2$(DMSO)$_4$] features *cis*-equatorial Cl atoms, one axial DMSO molecule *O*-coordinated, the other three *S*-coordinated (Scheme 1).[41] Hence, this *cis,fac* isomer will be denoted as RuCl$_2$(DMSO)$_4$ hereafter. See also ref.[42] for other NMR solution studies.

[41] E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sara, S. Zorzet, *Inorg. Chem.* **1998**, *27*, 4099.

[42] [42a] J. R. Barnes, R. J. Goodfellow, *J. Chem. Res. (S)* **1979**, 350. [42b] G. A. Heath, A. J. Lindsay, T. A. Stephenson, *J. Chem. Soc., Dalton Trans.* **1982**, 2429.

[43] *Spartan 5.1*, Wavefunction, Inc., 18401 Von Karman Ave., Ste. 370, Irvine, CA 92612, USA.

[44] J. J. Rack, H. B. Gray, *Inorg. Chem.* **1999**, *38*, 2, and references therein.

[45] An alternative modelling might employ the concept of locally dense basis sets,[46] i. e. featuring a high-quality basis set only on the atom whose properties are being calculated (Ru in this case). However, in the case of polyoxometalates like α-[PW$_{11}$RuO$_{39}$(DMSO)]$^{5-}$, this approach would not bring any substantial improvement in terms of computing time for such systems (containing a large number of heavy atoms), where a limiting factor is the size of the environment of the atom under study.

[46] A. C. De Dios, *Prog. Nucl. Magn. Reson. Spectr.* **1996**, *29*, 229.

[47] A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, manuscript in preparation.

Received October 11, 2001
[I01409]