Transition Metal Complexes

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Dispersion Forces, Disproportionation, and Stable High-Valent Late Transition Metal Alkyls

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Abstract: *The transition metal tetra- and trinorbornyl bromide complexes, M(nor)$_4$ (M = Fe, Co, Ni) and Ni(nor)$_3$Br (nor = 1-bicyclo[2.2.1]hept-1-yl) and their homolytic fragmentations were studied computationally using hybrid density functional theory (DFT) at the B3PW91 and B3PW91-D3 dispersion-corrected levels. Experimental structures were well replicated; the dispersion correction resulted in shortened M–C bond lengths for the stable complexes, and it was found that Fe(nor)$_4$ receives a remarkable 45.9 kcal mol^{-1} stabilization from the dispersion effects whereas the tetragonalized Co(nor)$_4$ shows stabilization of 38.3 kcal mol^{-1}. Ni(nor)$_4$ was calculated to be highly tetragonalized with long Ni–C bonds, providing a rationale for its current synthetic inaccessibility. Isodesmic exchange evaluation for Fe(nor)$_4$ confirmed that dispersion force attraction between norbornyl substituents is fundamental to the stability of these species.*

The isolation of the metal tetranorbornyls, M(nor)$_4$, (1-nor = bicyclo[2.2.1]hept-1-yl, M = Ti, Hf, Zr, V, Cr, Mn, Fe, Co)[1] in 1972 was a seminal event in the chemistry of transition metal alkyls.[2] These venerable compounds display high stability, uniform stoichiometry and low-spin configurations but they are more noteworthy for the unusually high +4 oxidation state displayed by the manganese, iron and cobalt species. Co(nor)$_4$ remains the only homoleptic, σ-bonded cobalt alkyl to have been characterized. Other stable homoleptic, open-shell, late transition metal alkyls are limited to a handful of neutral manganese(II) and iron(II) alkyls MnR$_2$ (R = -CH$_2$Bu^t,[3] -CH(SiMe$_3$)$_2$[4] or -C(SiMe$_3$)$_3$[5]) and Fe{C(SiMe$_3$)$_3$}$_2$[6] as well as the M^{I} complexes [M{C(SiMe$_3$)$_3$}$_2$]$^-$ (M = Mn and Fe)[7] and σ/π bonded [Co{C(SiMe$_2$Ph)$_3$}]$_2$.[8]

Subsequently, Co(nor)$_4$ and Fe(nor)$_4$ were resynthesized and spectroscopically and structurally characterized by the groups of Theopold[9] and Hayton,[10] and Mo(nor)$_4$ was also reported.[11] Hayton, Figueroa and co-workers described the related homoleptic M^{IV} species, M(N=C^{t}Bu$_2$)$_4$ (M = Co,[12] Fe[10]). In addition, Dimitrov and Linden characterized a related trinorbornyl nickel bromide and noted the number of short H···H contacts in the crystal structure.[13] Further work by Theopold and co-workers showed that both the anionic Co^{III} and cationic Co^{V} derivatives of Co(nor)$_4$ readily revert to the neutral Co(nor)$_4$, further underlining the unusually high stability of its +4 oxidation state.[14]

The stability of the tetranorbornyls is generally considered to be due to the preclusion of β-hydrogen elimination which yields a highly strained olefin and the reluctance of substituents at the bridgehead atom to undergo homolysis or nucleophilic displacement.[1] This, however, does not account for the ready formation of M(nor)$_4$ species from lower valent precursors, the shortened M–C bond lengths or their remarkable low-spin tetrahedral electronic configuration.

Recently there has been an increasing awareness of the importance of attractive London dispersion forces between C–H moieties of hydrocarbon groups in stabilizing species with sterically bulky substituents.[15] This work has been greatly facilitated by the development of low-cost quantum chemical methods to calculate dispersion force stabilization.[16] The calculations also showed that dispersion interactions are enhanced between rigid hydrocarbon groups,[17] which enable them to stabilize molecules with long C–C bonds.[18] The stability of several transition metal species has been rationalized on the basis of London dispersion forces involving C–H interactions.[19]

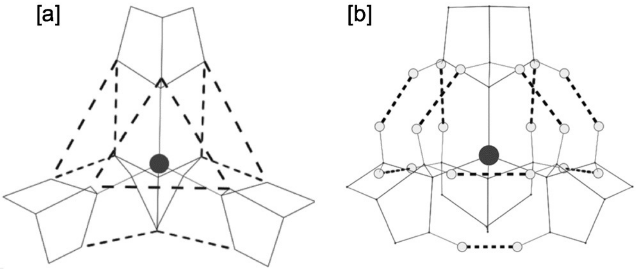

Figure 1. The crystallographically characterized structures of M(nor)$_4$ (M = Fe [a]; Co [b] (black circles)) showing C---C contacts under 3.6 Å [a] and H---H contacts under 2.4 Å [b], respectively (dashed lines).

Herein we describe the results of DFT calculations, both with and without dispersion corrections indicating that the stability and electronic structures of the homoleptic tetranorbornyl transition metal complexes are mainly a consequence of attractive London dispersion forces between the rigid norbornyl substituents.

The calculated structural parameters for M(nor)$_4$ (M = Fe, Co, Ni) and Ni(nor)$_3$Br at various levels of optimization are shown in Table 1 and Table 2 respectively. The currently unknown Ni(nor)$_4$ was also subjected to optimization applying initial coordinates derived from the cobalt congener.

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Table 1: Selected calculated structural parameters for M(nor)$_4$ (M = Fe, Co, Ni).

M	Fe			Co			Ni	
	B3PW91	-D3	Exp.[10]	B3PW91	-D3	Exp.[9]	B3PW91	-D3
M-C [Å]	1.939 (av.)	1.910 (av.)	1.993 (av.)	1.976 (av.)	1.942 (av.)	1.920 (av.)	2.009 (av.)	2.016 (av.)
C-M-C [°]	109.5 (av.) 109.3, 108.4, 111.0, 110.7, 108.9, 108.6	109.5 (av.) 109.5, 108.3, 110.8, 110.5, 109.0, 108.7	109.5 (av.) 109.4, 109.0, 109.7, 109.4, 109.8, 109.7	109.6 (av.) 111.8, 114.1, 97.8, 97.2, 119.2, 117.6	109.7 (av.) 119.3, 116.6, 97.0, 97.0, 114.6, 113.6	109.5 (av.) 113.4, 106.9, 106.9, 109.0, 109.0, 111.7	109.4 (av.) 95.7, 117.2, 108.4, 108.0, 116.8, 110.4	109.4 (av.) 94.9, 115.5, 109.8, 109.7, 115.6, 110.7

Table 2: Selected calculated structural parameters for Ni(nor)$_3$Br.

	B3PW91	-D3	Exp.[13]
Ni-C [Å]	1.926 (av.)	1.903 (av.)	1.933 (av.)
Ni-Br [Å]	2.383	2.361	2.386
C-Ni-C [°]	98.8, 101.9, 100.6	98.0, 101.0, 99.6	98.2, 101.8, 100.1
C-Ni-Br	112.6, 116.2, 123.5	113.2, 116.0, 125.2	113.4, 116.1, 123.8

Table 3: Selected calculated thermodynamic parameters for the heterolytic cleavage of three norbornyl ligands from M(nor)$_4$ (M = Fe, Co) and Ni(nor)$_3$Br (kcal mol^{-1}).

	$\mathrm{M(nor)_3X \rightarrow MX + 3\,nor}$					
	Fe(nor)$_4$		Co(nor)$_4$		Ni(nor)$_3$Br	
	B3PW91	-D3	B3PW91	-D3	B3PW91	-D3
ΔE[a]	112.8	159.1	104.1	146.9	116.6	154.1
ΔE[b]	111.9	157.8 (45.9)[d] (33.8)[e]	92.5	130.8 (38.3)[d]	102.1	138.9 (36.8)[d]
ΔH	111.8	158.0	92.2	130.7	102.0	138.9
$-T\Delta S$[c]	−42.5	−43.6	−41.1	−41.3	−39.1	−39.5
ΔG[c]	69.3	114.4	51.1	89.4	62.9	99.4

[a] Dissociation energy (kcal mol^{-1}). [b] With ZPE and BSSE correction. [c] At 298 K, 1 atm. [d] Dispersion stabilization (kcal mol^{-1}). [e] Calculated at the TPSS(-D3BJ) level (see the Supporting Information).

Calculations both with and without dispersion correction reproduce the crystallographically characterized structures with fair accuracy (it should be borne in mind that the calculations relate to gas phase molecules, which ignore intermolecular interactions that occur in the crystal). In Ni(nor)$_3$Br the unsymmetrical disposition of the norbornyls is well reproduced. Calculations on the structurally characterized tetranorbornyls show a slightly greater deviation from the crystallographic data, however both the corrected and uncorrected bond lengths in M(nor)$_4$ (M = Fe, Co) are within reasonable agreement. While the iron congener has consistently shorter M−C bond lengths than those observed via crystallography, the cobalt species shows consistently longer bonds. These deviations however are small and the latter is likely a reflection of the increased tetragonalization seen for the calculated cobalt structure compared to the experimental.

This tetragonalization lowers the local symmetry at the metal atom in contrast to the almost perfectly tetrahedral FeC$_4$ moiety, a distortion also seen in $\mathrm{Co(N{=}C{}^{t}Bu_2)_4}$.[12] Gratifyingly, these variations are present in the calculations however their magnitudes are much greater than those seen in the experimental data. The data are also informative as to the instability of Ni(nor)$_4$; Dimitrov and Linden reported that the reaction of Ni(nor)$_3$Br with 1-norbornyl lithium gave only dinorbornane and noted that such a salt metathesis did not provide access to Ni(nor)$_4$.[13] The elongation of the Ni−C bonds as well as the C-Ni-C angles in this species relative to Ni(nor)$_3$Br hint at the source of this instability, for the calculated structure of Ni(nor)$_4$ is shown to have one very narrow C-Ni-C angle of 94.9°. Thus, the long bonds and the close approach of two of the norbornyl ligands is likely to predispose the complex to reductive elimination, yielding a highly reactive, unobserved, nickel(II) dialkyl, and the observed dinorbornane.

The thermodynamic parameters for the homolytic dissociation of three of the norbornyl ligands of M(nor)$_4$ (M = Fe, Co) and Ni(nor)$_3$Br were calculated with and without dispersion correction and are summarized in Table 3. It is evident from these data that dispersion forces have a significant influence upon the stability of both the metal tetranorbornyls and nickel trinorbornyl bromide with stabilization energies ranging from 45.9 to 36.8 kcal mol^{-1}. The uncorrected values calculated are also informative, indicating a higher stability of the iron species relative to the cobalt. Decreased steric clash induced by the tetrahedral Fe(nor)$_4$ relative to tetragonalized Co(nor)$_4$ alongside the higher covalent radius of Fe are likely to favor increased stability for this species. The increased strength of Fe−C bonds relative to Co−C bonds, consistent with the relative dearth of cobalt hydrocarbyls, also contributes. Further evidence for the effects of steric clash in the uncorrected values can be seen in Ni(nor)$_3$Br which shows a higher stability to loss of the norbornyl ligands than the related Co(nor)$_4$ by 12.5 kcal mol^{-1} in spite of its similarly distorted structure. Although weaker Ni−C bonds would be expected, the reduced steric congestion induced by the replacement of one norbornyl ligand with bromide is the source of this effect.

The energy of the stabilization provided by London dispersion effects contributes significantly to the stability of these unusually high oxidation state compounds in all cases. Fe(nor)$_4$ receives the greatest stabilization of 45.9 kcal mol^{-1}, likely a consequence of its tetrahedral conformation which optimizes short contacts between the norbornyl ligands. In contrast, the tetragonalization of the cobalt species both increases steric clash, as shown by the uncorrected values, and decreases the efficacy of the dispersion interactions yielding a lower 38.3 kcal mol^{-1} stabilization. This value must be treated with caution owing to the deviation of the calculated and experimental structures however the tetragonalization of the cobalt congener evidently reduces its stability. Reassessment of the iron congener at the TPSS-(D3BJ) level gives a somewhat reduced but still high stabilization energy of 33.8 kcal mol^{-1}, an observation consistent with the model-dependence of dispersion correction methods.[20]

For Ni(nor)$_3$Br, the dispersion stabilization of 36.8 kcal mol^{-1} provides strong evidence for the efficacy of the norbornyl ligand in contributing attractive dispersion forces to stabilizing a structure. The dispersion stabilization calculated for the cobalt tetranorbornyl and nickel tris(1-norbornyl) bromide are very similar. This reflects the high structural dependence of dispersion forces; the tetragonalization in Co(nor)$_4$ is sufficient to decrease the attractive dispersion forces between the ligands to a level similar to one norbornyl being exchanged for a less dispersive bromide ligand as is the case in Ni(nor)$_3$Br.

These data are in harmony with the empirically observed enhanced stability of Fe(nor)$_4$ and Ni(nor)$_3$Br relative to Co(nor)$_4$ and thus are unlikely to be an artefact of the calculations. Bower and Tennent reported that Fe(nor)$_4$ is far more stable to both hydrolysis and oxidative degradation than its cobalt analogue while Dimitrov and Linden report Ni(nor)$_3$Br to be stable in air for a number of days and that its degradation temperature is high.

In order to corroborate data derived from a stepwise dissociative methodology, the more widely applied isodesmic exchange reaction was attempted for the Fe(nor)$_4$ (Figure 2).

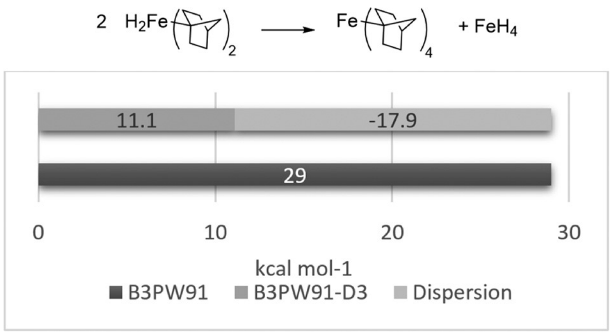

Figure 2. The results of an isodesmic exchange calculation regarding Fe(nor)$_4$.

This isodesmic exchange describes the putative conversion of two iron dinorbornyl dihydrides to Fe(nor)$_4$ and FeH$_4$. Each side of this theoretical reaction contain an identical number of each type of Fe−X bond and thus the effect of dispersion interactions between the ligands can be assessed.[21]

The calculated value of −17.9 kcal mol^{-1} reflects the conversion of 2 nor-nor interactions in the putative Fe(nor)$_2$H$_2$ to 5 new nor-nor interactions in Fe(nor)$_4$ (6 in total less that originally in Fe(nor)$_2$H$_2$). The dissociative approach converts 6 nor–nor interactions to 0, and thus the observed value around $^2/_5$ of that from the dissociative approach shows excellent correlation. These data indicate the validity of the dissociative assessment, and strongly imply that the dominant dispersion force stabilization arises from ligand–ligand interactions (see the Supporting Information).

The main conclusion from the calculations is that dispersion effects are key for the stability of metal tetra- and trinorbornyl halide species. The large number of short interligand H⋯H contacts in the compounds reflect an enhanced dispersion force stabilization of up to 45.9 kcal mol^{-1} for the homolytic cleavage of the norbornyl ligands. Isodesmic exchange analysis closely mirrors these data indicating the validity of this dissociative analysis. The stability seen in these molecules arises from the harmonious combination of steric and dispersion force effects of the four 1-norbornyl groups which occupy the metal environment and maximize the dispersion force attraction between them.

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