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Electronic Effects on the Stability of Isomeric Alkyl Transition Metal Compounds[‡]

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Density functional calculations on a variety of alkyl−transition metal complexes R−M are reported. Specifically, the following compounds have been studied: zirconocene complexes [$Cp_2Zr(H)R$], [$Cp_2Zr(Cl)R$], [Cp_2ZrR]$^+$, and [$Cp^*{}_2Zr(Cl)R$]; iron compounds [$CpFe(CO)_2R$] and [CpFe(CO) {$P(CH_3)_3$}]; dimethylamino−dithiocyanato−palladium complexes [{$(CH_3)_2NCS_2$}-Pd{$P(CH_3)_3$}R]; and cationic diimino palladium complexes [{**NN**}Pd(L)R]+ (with {**NN**} = HN═CH−CH═NH or *N*,*N*′-(*o*,*o*′-bis-diisopropylphenyl)diiminoacenaphthalene, and L = nothing, Cl^-, $(CH_3)_2O$, $(CH_3)_2S$, C_2H_4, or CH_3CN). The R groups considered are methyl, *n*-propyl, isobutyl, isopropyl, and *tert*-butyl, thus covering the whole range from primary groups to tertiary ones. It is shown that primary alkyl complexes are usually more stable than secondary and tertiary ones and that this is an *electronic* effect, due to the partial carbanionic character of the alkyl group. Steric effects, which are usually invoked in the literature whenever this issue is considered, are shown to play only a minor role in many cases. Notable exceptions occur in the case of extremely bulky compounds or for systems in which the metal−carbon bond is less polar.

Introduction

Alkyl−transition metal compounds are important intermediates in a number of catalytic processes, including polymerization. Unlike most main group alkyl compounds, these species often undergo relatively facile isomerization of the alkyl group (Figure 1). This is due to the availability of low-energy pathways such as the three-step mechanism involving β-hydride transfer to metal to form a hydrido−alkene complex, rotation of the alkene, and reinsertion to form the isomeric alkyl−metal. Consequently, this type of reaction is often observed and plays an important—detrimental or on the contrary rather useful—role in determining the selectivity of the process involved.

Homogeneous polymerization of alkenes by zirconium(IV), nickel(II), or palladium(II) complexes is an example of a process that has been of much recent interest and in which the alkylmetal intermediates can undergo isomerization. The rate and position of the equilibrium of this isomerization, relative to the rate of the chain-lengthening and -termination steps, can influence the degree of branching and the tacticity of the polymer formed. By varying the conditions (temperature, concentration of alkene, nature of ligands), these factors can be controlled. For example, polymerization of α-alkenes with α-diimine nickel(II) catalysts can be regulated to lead to polymer with a considerable degree of chain-*straightening*,[1] whereas polymerization of ethylene with the same catalysts can be used to generate *branched* polyethylene.[2]

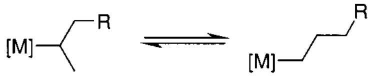

Figure 1. Isomerization of alkyl−metal compounds.

Where equilibria between isomeric alkyl−metal compounds have been observed, the favored isomer has often, although not always, involved a terminal or primary alkyl group, with secondary or tertiary isomers present either in small amounts or not at all. This has usually been attributed to a *steric* effect: in crowded coordination compounds, secondary and especially tertiary groups can be expected to undergo more repulsive interactions with neighboring ligands than primary ones. However, this strong focus on the role of steric effects, important as they are, neglects the fact that there is an equally or even more important *electronic* effect. The reason for which this second effect has often been overlooked is that it usually operates in the same direction as the first one. Where a metal−carbon bond has a strong ionic character ($M^{\delta+}-C^{\delta-}$), primary alkyl groups will be favored, because of the inductive electron-releasing effect of the alkyl substituents on the α-carbon atom. Expressed simply, primary carbanions are more stable than secondary ones, which in turn are more stable than tertiary ones (and the methyl anion is more stable than any of them). In a set of elegant studies, Reger et al. have demonstrated that the position of the equilibrium in a set of (dithiocarbamato)(trialkylphosphine) palladium and platinum(II) alkyl compounds is defined almost entirely by the *electronic* effect, with steric effects apparently playing a negligible role.[3] Thus,

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(1) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665.

(2) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320−2334.

(3) (a) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1991**, *10*, 902−906. (b) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1992**, *11*, 4285−4292. (c) Reger, D. L.; Ding, Y.; Garza, D. G.; Lebioda, L. *J. Organomet. Chem.* **1993**, *452*, 263−270.

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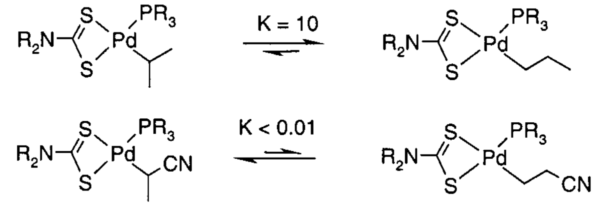

Figure 2. Isomerization equilibria of dithiocarbamato palladium complexes.

the linear *n*-propyl complex is more stable than its isopropyl isomer, whereas the *branched* α-cyanoethyl complex is more stable than its isomer, due to the stabilizing interaction between the cyano group and the partial negative charge on the neighboring carbon atom. (Figure 2).

In the discussion above, the relative stability of isomeric alkylmetals has been seen to depend on the polarity of the metal−carbon bond. This dependence is general for all alkyl−element compounds and, for main group compounds, is in fact a fairly well-known general principle of physical organic chemistry: electronegative groups bind preferentially to tertiary and secondary alkyl groups; electropositive groups prefer methyl and primary alkyl groups. This correlation was first pointed out as early as 1968[4] and has been much discussed since.[5−7] Its origin has been variously ascribed to electronegativity effects,[5c,g,6] to electrostatic interactions between partial charges,[5a,h,i] to repulsion between C−H bonds,[6c] and more recently to orbital phase effects.[5k] From the practical point of view pursued here, since all these explanations are consistent in terms of their predictions, they can be taken to be fundamentally equivalent. Typical energy differences between primary and secondary alkyl compounds due to this effect can be on the order of 1−5 kcal/mol, more than enough to strongly affect the position of an equilibrium. The best characterized organometallic systems are the alkyllithium compounds, where, for example, *n*-butyllithium is found, both experimentally[8] and computationally,[9] to be ca. 2.5 kcal/mol more stable than its secondary isomer.

For transition metal alkyls relevant to catalysis, accurate thermochemical data are of course much less forthcoming;[10] however, the general trend that primary alkyl compounds are more stable than secondary ones is supported by a large amount of data. As discussed above, this is usually attributed to steric effects. The strongest evidence against this interpretation comes mostly from considering equilibria involving alkyl groups with electron-withdrawing substituents such as cyano or phenyl groups, which should be able to stabilize partial negative charges in the branched isomers, where the substituent is bonded directly to the metal-bound carbon atom. In this case, the electronic and steric effects act in *opposite* directions. As well as for the palladium complexes of Reger et al. discussed above, electronic effects have been shown to dominate in the equilibria of isomers of alkyl−rhodium porphyrin compounds.[11] Thus, the branched isomer [Rh(ttp)CH(Ph)-(CH_3)] is favored with $K = 7.5$ over the linear isomer [Rh(ttp)CH_2CH_2Ph], whereas the isopropyl complex is disfavored with respect to the linear *n*-propyl isomer, with $K = 0.7$.

Overall, this effect is not very well known among organometallic chemists. Due to the difficulties in obtaining enough accurate experimental data, its importance is unclear, in particular the extent to which electronic or steric effects account for the commonly observed preference for primary alkyl compounds. More subtle substituent effects, such as the dependence on the nature of the metal atom, on the oxidation state involved, and on the electronic properties of the other ligands on the metal, have barely been considered.

In this study, the relative energy of isomeric alkyl complexes of three transition metals has been studied using computational methods.[12] By varying the metal and the ligands, the relative role of steric and electronic effects can be explored in a controlled manner. As well as a reference system, the alkyllithium compounds, four classes of transition metal complexes, covering early, mid, and late transition metals, and a variety of ligands have been chosen: (1) zirconocene derivatives [$(Cp)_2$Zr-(X)R], where X is either H, Cl, or a positive charge; (2) iron(II) complexes [CpFe(CO)(L)(R)], where L = CO or PMe_3; (3) the palladium(II) complexes [{R_2NCS_2}Pd-(PR_3)(R)] studied in detail by Reger et al.;[3] and (4) the diimine palladium(II) complexes [(diimine)Pd^+(X)(R)] studied by Brookhart et al.[13]

Density-functional theory (DFT), together with the very commonly used B3LYP hybrid functional, was used for all the computations described here. This approach has proved to be extremely effective where transition metal compounds are involved, due to its moderate computational cost and high accuracy—much better than Hartree−Fock techniques, and often considerably better than correlated techniques such as MP2.[12] For some of the larger complexes treated here, previous studies have made use of QM/MM techniques,[14] treating the "reactive" core, containing the metal atom, the atoms bonded to it, and some others, using a quantum-

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[4] Robinson, G. C. *J. Org. Chem.* **1968**, *32*, 1963−1965.

[5] (a) Benson, S. W.; Luria, M. *J. Am. Chem. Soc.* **1975**, *97*, 704−709. (b) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412−4419. (c) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255−5257. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *12*, 1647−1660. (e) Wiberg, K. B. *J. Org. Chem.* **1991**, *56*, 544−550. (f) Laidig, K. E. *J. Phys. Chem.* **1991**, *95*, 7709−7713. (g) Luo, Y.-R.; Benson, S. W. *Acc. Chem. Res.* **1992**, *25*, 375−381. (h) Laurencelle, N.; Pacey, P. D. *J. Am. Chem. Soc.* **1993**, *115*, 625−631. (i) Luo, Y.-R.; Pacey, P. D. *Can. J. Chem.* **1993**, *71*, 572−577. (j) Leroy, G.; Dewispelaere, J.-P.; Wilante, C. *J. Mol. Struct. (THEOCHEM)* **1998**, *433*, 239−245. (k) Ma, J.; Inagaki, S. *J. Am. Chem. Soc.* **2001**, *123*, 1193−1198.

[6] (a) Smith, D. W. *Aust. J. Chem.* **1995**, *48*, 65−77. (b) Smith, D. W. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 201−205. (c) Smith, D. W. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4065−4068. (d) Smith, D. W. *J. Organomet. Chem.* **1999**, *585*, 150−153.

[7] For a review, see: Harvey, J. N.; Viehe, H. G. *J. Prakt. Chem.* **1995**, *337*, 253−265.

[8] Arnett, E. M.; Moe, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 7068−7069.

[9] Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129−1140.

[10] For some limited data, see e.g.: Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688. Drago, R. S.; Wong, N. M.; Ferris, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 91−98.

[11] Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686. Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, 3333−3334.

[12] For reviews on application of computational chemistry to organometallic chemistry, see: (a) The special issue: *Chem. Rev.* **2000**, *100*, 351. (b) *Computational Organometallic Chemistry*; Cundari, T. R., Ed.; Marcel Dekker: New York, 2001.

[13] Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686−6700.

[14] Maseras, F. *Chem. Commun.* **2000**, *19*, 1821−1827.

mechanical technique such as DFT, and the rest of the atoms using a molecular mechanics scheme. While this has undeniable computational benefits, and also enables some discrimination between electronic and steric effects, it is a more approximate method than purely QM computations and may therefore not be suitable for reproducing the very small energy differences of interest in this study. The same point about QM/MM techniques has been made in a similar context before.[15] For the present study, where only minima are considered, so that geometry optimization is straightforward and the computational effort is not too high, it turns out that full B3LYP optimization of all species using adequate basis sets is well within the reach of standard computational resources.

Computational Details

Geometry optimization of all species discussed here was carried out at the B3LYP level of theory, using flexible basis sets. All computations were performed using pseudospectral methods together with the Jaguar program package.[16] The principle used in choosing the basis sets was to minimize computational expense while simultaneously treating the metal atom and its immediate environment as accurately as possible. The zirconium, iron, and palladium atoms were described with Los Alamos effective core potentials so as to reduce the number of electrons and account for scalar relativistic effects. The explicitly described *n*s, *n*p, *n*d (and $n + 1$s, $n = 3$ for Fe, 4 for Zr and Pd) electrons were treated with the triple-ζ contraction developed for use with Jaguar (LACV3P basis).[16] All the other atoms used the double-ζ standard 6-31G basis, with extra polarization or diffuse functions in some cases. Specifically, the lithium atom as well as the whole of the metal-bound alkyl groups, and the metal-bound hydride, were described with the 6-31G** basis; the fluorine and chlorine atoms used the 6-31+G* basis; the Cp (C_5H_5) and Cp* ($C_5(CH_3)_5$) rings used the 6-31G* basis, except that no polarization function was present on the C atoms of the methyl groups in Cp*; for the palladium complexes, only the four atoms of the diimine N=C−C=N backbone had polarization functions (6-31G* basis), whereas the acenaphthalene and 2,6-bis(isopropyl)phenyl groups were treated with the 6-31G basis. All atoms in the CH_3CN, $(CH_3)_2O$, ethylene, and $(CH_3)_2S$ ligands were treated with the 6-31G* basis, except for the sulfur atom in the dimethyl sulfide, where the triple-ζ 6-311G* basis was used instead. In all cases, only the five spherical harmonic components of the d functions were used. The effect of using a larger basis set was monitored in the case of the $[\{R_2NCS_2\}Pd\{P(CH_3)_3\}R]$ complexes: Supplementary diffuse functions were added on Pd (LACV3P++ basis), and the double-ζ 6-31G basis for other atoms was replaced with the triple-ζ basis on other atoms (6-311++G** on the metal-bound alkyl group, 6-311+G* on other atoms). Single-point energies with this basis are referred to below as B3LYP/BSII.

For the larger compounds, the Jaguar “loose” geometry optimization criteria (i.e., the rms gradient was required to be below 1.5×10^{-3} hartree/bohr) were used; test calculations showed that results obtained with the tighter standard thresholds were essentially identical, in terms of both energies and bond lengths and angles. For the most part, even the largest molecules studied here have fairly well defined structural properties, so that it is possible to predict the approximate geometry of the overall minimum simply by inspection and to initiate geometry optimization from that point. However, wherever any doubt was possible, which was especially common in the case of the diimino palladium complexes, several starting geometries were used; the data in the Tables and the Supplementary Information refer in every case to the lowest energy isomer found. Standard DFT and pseudospectral integration grids were used for geometry optimization, with fine grids and tighter cutoffs for the final energy calculation. The expected accuracy of B3LYP for quantities such as bond energies is roughly ±5 kcal/mol. However, the energies considered here are *relative* energies, so that much of the error should cancel, and on a reasonable estimate, the error on the energies quoted below should not exceed 1 kcal/mol. Finally, all the reaction energies reported here are based on electronic energies, without correction for zero-point energy (ZPE). Frequency calculations on large molecules such as described here are extremely time-consuming, and given the similarity between the compounds considered, the effect of ZPE is expected to be small. To test this, harmonic frequencies were computed at the Hartree−Fock level of theory (which yields geometries similar to the B3LYP method) for the two propyl isomers of $[Cp_2Zr(H)(C_3H_7)]$. The computed ZPEs are 179.93 and 179.89 kcal/mol.

To analyze the nature of the metal−carbon bond, natural population analysis[17] (NPA) is used to determine charges on the metal atom and the alkyl groups.

Results and Discussion

As discussed above, our focus is on the *relative stability* of isomeric alkylmetal compounds. Stability can be measured in many ways, depending on which reference system is chosen. Perhaps the most natural measure for the present case would be the metal−carbon energy, and this has indeed been used in several previous studies which have addressed the issue of isomerization energetics. However, isomeric alkyl radicals themselves differ in energy, with isopropyl more stable than *n*-propyl by roughly 4 kcal/mol at the level of theory used here. This means, for example, that isoenergetic linear and branched propyl complexes have substantially *different* M−C bond energies. Also, it is not always easy to deconvolute steric and electronic effects on bond energies. A more appropriate measure of stability in the present context, where it is specifically the relative stability of different alkyl derivatives that is of interest, is the *methyl−alkyl transfer stabilization energy* (MSE),[5d] defined as the energy change[18] corresponding to reaction 1, where [M] is the metal group involved.

$$R{-}[M] + CH_4 \rightarrow R{-}H + CH_3{-}[M] \qquad (1)$$

Positive values of the MSE correspond to alkyl−metal species which are *more* stable than the corresponding methyl derivative, and negative values to less stable ones. We will interpret the MSE data by reference to the computed MSEs of the alkyllithium data. *Systematic* deviation from these values will be attributed to electronic effects. For example, the lithium MSE for all alkyllithium compounds is negative, because methyllithium is more stable than any of the others. Therefore,

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[15] Michalak, A.; Ziegler, T. *Organometallics* **2000**, *19*, 1850.

[16] *Jaguar 4.0*; Schrödinger, Inc.: Portland, OR, 1991−2000.

[17] (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) For a discussion of the application of natural bonding orbital methods to transition metal compounds, see: Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717−774.

[18] The position of the equilibrium in hypothetical isomerization reactions would of course depend on the relative *free* energies instead of electronic energies. However, the zero-point energy, internal vibrational energy, and entropy effects can be assumed to be rather small and should mostly cancel out in these isodesmic reactions.

Table 1. Calculated Methyl Alkyl Transfer Stabilization Energies (MSEs, kcal/mol) of Alkyllithium Compounds and NPA Charges *Q* on the Alkyl Group

R	MSE (RLi)	*Q*(R)
methyl	0.00	−0.754
n-propyl	−3.09	−0.733
isopropyl	−6.79	−0.725
isobutyl	−2.81	−0.748
tert-butyl	−8.15	−0.731

positive MSEs for alkylmetal compounds will be an indication that the metal prefers to bond to more electron-donating alkyl groups. Deviation from the lithium MSEs only for the larger, bulkier groups will be interpreted as due to steric effects. In this way, the consideration of MSEs allows electronic and steric effects to be distinguished in an at least partially objective way purely on the basis of energetic data and without recourse to structural considerations. This is important because it is usually only where there is a large steric destabilization that obvious signs of strain can be detected in the structure. For smaller steric effects (<5 kcal/mol), this is much more difficult, with the structures often found to be rather similar to those of the unhindered species.

Given the large number of compounds surveyed, the amount of thermochemical and structural information potentially available from our study is considerably larger than the subset on which the primary focus is laid in this study, namely, the MSEs. For the sake of brevity, and to avoid repetition of data already discussed elsewhere, other energetic data will not be discussed, but all total energies and Cartesian coordinates of all the species studied are available as Supplementary Information. For similar reasons of brevity and focus, a deliberate decision *not* to discuss any aspect of the isomerization mechanisms was taken. For some of the systems, other computational work has considered this, and appropriate references can be found in the text.

1. Alkyllithium Compounds. These are included for comparison purposes, since their thermochemistry is well established from previous computations[19] and experiment.[20] The order of stability of the methyl, *n*-propyl, isopropyl, isobutyl, and *tert*-butyl alkyllithium compounds can be taken as a reference for the stability of highly ionic alkylmetal compounds in which steric effects play no role.[21] As can be seen in Table 1, methyllithium is the most stable compound, followed by the primary, secondary, and tertiary alkyl derivatives, in that order. The energy differences are in line with those obtained previously[19] and can all be understood in terms of the difference in electronegativity between C, Li, and H: Lithium "prefers" to bond to the more electronegative alkyl groups, i.e., to methyl or primary alkyl groups such as *n*-propyl or isobutyl.

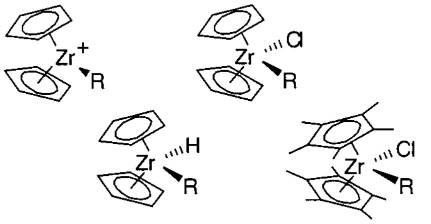

Figure 3. Alkyl−zirconocene species computed in this study.

Lithium is a highly electropositive element, so the bonding can be expected to be highly ionic. This is confirmed by natural population analysis,[17] as can be seen by the positive charges on lithium in Table 1, which are uniformly large, although significantly smaller than 1, indicating at least a degree of covalent bonding.

2. Alkyl−Zirconocenes. These complexes are important both in the Schwartz hydrozirconation method for terminal functionalization of alkenes[22] and in homogeneous polymerization. Zirconium is a rather electropositive metal, which should also have rather "ionic" bonding to carbon. Due to the strong interest in zirconocenes as polymerization catalysts, a very large number of computational studies have been carried out on various cationic derivatives $[Cp_2ZrR]^+$, with a particular focus on the mechanistic aspects of the polymerization.[23,24] Several of the studies are particularly relevant because they treated the energetic or mechanistic aspects of isomerization.[23f,h,i] In contrast to this abundance of studies on cationic species, only one study has addressed the chloro compounds and the hydrozirconation reaction,[25] but did not study isomeric species.

In this study, a range of Zr(IV) zirconocenes have been considered (see Figure 3), including the cationic species that are relevant to the polymerization catalysts and the hydrido and chloro compounds involved in the alkene rearrangement reactions. To assess the steric effects, methyl, *n*-propyl, isopropyl, isobutyl, and *tert*-butyl compounds have been considered. For the most highly sterically congested chloro compounds, both the standard zirconocene $[Cp_2ZrCl]$ and the permethylated $[Cp^*{}_2ZrCl]$ have been considered.

The MSEs for these compounds are summarized in Table 2. As in the case of the alkyllithiums, the interpretation of the data in Table 2 is for the most part

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[19] Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *34*, 1129−1140, and references therein.

[20] Arnett, E. M.; Moe, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 7068−7069.

[21] Note that "bare" transition metal−alkyl compounds, in which the metal atom bears no or few ligands, and which are therefore very similar to the alkyllithiums, can be made in the gas phase. There is much indirect evidence that the preference for primary positions is found here too. This has been established in at least one case by computation: Perry, J. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994**, *116*, 5013−5014.

[22] (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Chirik, P. J.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 10308−10317.

[23] Selected references: (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742. (b) Castonguay, L. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 5832−5842. (c) Kawamura-Kuribayashi H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687−8694. (d) Meier, R. J.; van Doremaele, G. H. J.; Iarlori, S.; Buda, F. *J. Am. Chem. Soc.* **1994**, *116*, 7274−7281. (e) Cruz, V. L.; Muñoz-Escalona, A.; Martinez-Salazar, J. *Polymer* **1996**, *37*, 1663−1667. (f) Prosenc, M.-H.; Brintzinger, H.-H. *Organometallics* **1997**, *16*, 3889−3894. (g) Margl, P.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1998**, *120*, 5517−5525. (h) Moscardi, G.; Thorshaug, K.; Støvneng, J. A.; Rytter, E.; Ystenes, M. *Macromolecules* **1998**, *31*, 7149−7165. (i) Lohrenz, J. C. W.; Bühl, M.; Weber, M.; Thiel, W. *J. Organomet. Chem.* **1999**, *592*, 11−21. (j) Chan, M. S. W.; Ziegler, T. *Organometallics* **2000**, *19*, 5182−5189. (k) Resconi, L.; Cavallo, L. *Organometallics* **2001**, *20*, 1918−1931.

[24] For reviews on computational studies of homogeneous polymerization catalysis, see ref 12: (a) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823−842. (b) Musaev, D. G.; Morokuma, K. *Adv. Chem. Phys.* **1996**, *95*, 61−128. (c) Woo, T. K.; Margl, P. M.; Deng, L.; Cavallo, L.; Ziegler, T. *Catal. Today* **1999**, *50*, 479−500. (d) Rappé, A. K.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435−1456.

[25] Endo, J.; Koga, N.; Morokuma, K. *Organometallics* **1993**, *12*, 2777−2787.

Table 2. Calculated Methyl Alkyl Transfer Stabilization Energies (MSEs, kcal/mol) of Alkyl Zirconocene Compounds and NPA Charge on the Alkyl Group in the [$Cp_2Zr(Cl)R$] Complexes

R	MSE [$Cp_2Zr(H)R$]	MSE [$Cp_2Zr(Cl)R$]	Q(R) in [$Cp_2Zr(Cl)R$]	MSE [Cp_2ZrR]$^+$	MSE [$Cp^*_2Zr(Cl)R$]
methyl	0.00	0.00	−0.445		0.00
n-propyl	−2.43	−2.69	−0.450	8.06	−6.54
isopropyl	−5.85	−6.13	−0.444	5.11	−13.58
isobutyl	−3.39	−4.68	−0.441	6.89	−11.49
tert-butyl	−10.75	−12.02	−0.456	0.34	−26.55

straightforward. Starting with the Cp,hydrido and Cp,chloro complexes, it can be seen that zirconium(IV) clearly bonds more strongly to the less branched alkyl groups. The energy differences between the methyl, *n*-propyl, and isopropyl derivatives are in fact rather similar to those found for the lithium compounds. However, the *tert*-butyl compound (and to a lesser extent the isobutyl one too) is more destabilized relative to methyl than would be expected from extrapolating the trends for the lithium compounds alone, which is presumably due to steric effects. The similarity to the lithium compounds extends to the fact that the bond is quite highly ionic, as shown by the NPA charges on the alkyl group in the chloro derivatives.

Turning to the cationic derivatives, it can be seen that all of the MSEs are positive. This is due to the favorable β-agostic interaction between the unfilled orbital on the metal and a C−H bond, an interaction that is absent in the methyl compound. Assuming that the stabilization due to this interaction is more or less constant for different alkyl groups, one can see that the same underlying trend in stability is found as for the hydride and chloride complexes. The steric destabilization of the isobutyl and *tert*-butyl compounds is apparently slightly smaller than in the tetrasubstituted derivatives, as one might have expected. It should be noted that in the *tert*-butyl complex only one of the β-methyl groups has an agostic interaction with the metal; an isomeric structure where two of the methyl groups interact in this way lies 1.9 kcal mol^{-1} higher in energy. The order of stability of these isomers is reversed with the BP86 density functional, in agreement with a previous study at that level which found the bis-β-agostic structure to be more stable by ca. 1 kcal/mol.[23f]

Finally, all of the permethylated alkyl derivatives [$Cp^*_2Zr(Cl)R$] are destabilized, in the case of the *tert*-butyl compound extremely so. This is the one example where the steric effect clearly shows up in the geometry. The carbon atoms of the cyclopentadiene ring situated close to the *tert*-butyl group are forced to move away from the metal in the compounds with the larger alkyl groups. Thus, the average Zr−C distance is 2.61 Å in the methyl compound, 2.62 Å in the *n*-propyl derivative, and 2.65 Å in the *tert*-butyl compound, with maximum values of 2.72 and 2.68 Å.

Overall, therefore, these zirconium compounds behave very similarly to the highly ionic alkyllithium derivatives. Except for the most bulky Cp* and *tert*-butyl substituents, there is no evidence for a significant steric contribution to the order of stability. This convincingly proves that the very high selectivity found in hydrozirconation reactions is due to the electronic preference of zirconocene compounds for primary alkyl groups and may also play a role in the stereoselectivity of propene polymerization by homogeneous zirconium catalysts.

Table 3. Calculated Methyl Alkyl Transfer Stabilization Energies (MSEs, kcal/mol) of Cyclopentadienyl Iron(II) Compounds [$CpFe(CO)(L)R$], L = CO, $P(CH_3)_3$, and the Overall NPA Charge on the Methyl Group in [$CpFe(CO)(L)CH_3$]

L/R	*n*-propyl	isopropyl	Q(Me)[a]
CO	−1.03	−2.54	−0.172
$P(CH_3)_3$	−2.97	−8.24	−0.254

[a] As can be seen in Tables 1 and 2, the computed charges on methyl are typical for all alkyl groups, and the others are therefore omitted henceforth for brevity.

3. Cyclopentadienyl Iron(II) Complexes. One of the first careful experiments concerning the isomerization of alkyl transition metal complexes was the study by Reger and Culbertson on [$CpFe(CO)(PPh_3)$(*n*-butyl)] and the secondary isomer.[26] The primary isomer is the only one observed at equilibrium, indicating a large energy difference. The [$CpFe(CO)_2R$] complexes are of interest too, because the more electron-withdrawing CO ligand should make the metal less "electropositive", which should mean that the primary isomer is less favored. A mixed complex [$CpFe(CO)_2-R-Fe(CO)_2Cp$] has been synthesized, in which the alkyl group bonds to one of the iron atoms in a primary position and to the other in a secondary position. The secondary group is found to be more reactive, consistent with it being less stable.[27]

To compare with these experiments, MSEs were calculated for the complexes [$CpFe(CO)(L)R$], L = CO, $P(CH_3)_3$. The smaller trimethylphosphine group was chosen instead of Ph_3P for computational convenience, and the butyl groups were replaced by propyl ones. The results in Table 3 are in agreement with experiment: the *n*-propyl complex is much more stable than the isopropyl derivative, especially in the case of the phosphine derivatives. The energy difference is smaller for the dicarbonyl complexes, consistent with electronic effects having a smaller role. The MSE of the isopropyl, phosphine complex is very slightly less stable than would be expected from electronic effects alone, indicating that steric effects may play some role.

The smaller MSEs in the dicarbonyl complexes must be due to the electron-withdrawing nature of the carbonyl group, leading to a less polar Fe−C bond, consistent with the smaller charge on methyl. This is clear evidence that the electronic effect favoring primary alkyl groups can be affected not only by the type of metal atom involved, but also by the ligands. A similar influence of the ligands on linear/branched alkyl energy differences has been observed in a number of other

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(26) (a) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789−2794. (b) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104−3107.

(27) Cammell, E. J.; Andersen, J.-A. M. *J. Organomet. Chem.* **2000**, *604*, 7−11.

Table 4. Calculated Methyl Alkyl Transfer Stabilization Energies (MSEs, kcal/mol) of Alkyl Palladium(II) Compounds and the Overall NPA Charge on the Alkyl Group and the MSEs Computed from Single-Point Calculations Using the Larger Basis Set BSII

R	MSE	*Q*(R)	MSE (BSII)
methyl	0.00	−0.249	0.00
n-propyl	−0.22	−0.223	−0.40
isopropyl	−1.00	−0.195	−0.82
isobutyl	−1.91	−0.224	−2.10
tert-butyl	−7.07	−0.179	−7.21
$-CH_2CH_2CN$	2.59	−0.286	2.90
$-CH(CH_3)CN$	9.71	−0.369	9.05
$-CH_2CH_2CF_3$	2.60	−0.288	2.10
$-CH(CH_3)(CF_3)$	3.05	−0.344	2.71

computational studies,[28] although it has not always been recognized as deriving from electronic effects.

4. Dithiocarbamatophosphinoalkyl Palladium(II) Complexes. This next set of compounds was the object of the careful isomerization studies[3] already discussed above and shown in Figure 2. The role of steric effects in these equilibria was suggested to be very small based on the observation that varying the phosphine groups did not substantially change the position of equilibrium.[3c] Also, the crystal structures show no close contacts in the branched isomers. For this case, as well as studying the simple alkyl groups, two heteroatom-substituted alkyl groups, cyanoethyl- and trifluoropropyl, have been included for comparison. There does not appear to have been any previous computational studies on any of these compounds.[29] However, X-ray structures are available for related $[\{(CH_2)_4NCS_2\}Pd\{P(C_2H_5)_3\}R]$ complexes.[3a] The geometries obtained here compare well with these experimental ones, although there is a systematic trend toward slightly longer palladium−element bond lengths. For example, the computed (experimental) lengths of the Pd−C and Pd−P bonds in the isopropyl compound are respectively 2.105 (2.074) and 2.293 (2.241) Å. These small geometric discrepancies should not affect the relative energies computed below.

The MSEs of the different alkyl groups for the complex $[\{(CH_3)_2NCS_2\}Pd^{(II)}\{P(CH_3)_3\}R]$ are shown in Table 4. First of all, it can be seen that the MSEs derived using single-point energy calculations with a larger basis set are very close to those obtained using the standard basis. In no case is there a difference between the two values that is large enough to be of any significance. This suggests that the MSEs computed here and in the other sections are fairly reliable.

It can further be seen that the calculated numbers are in good agreement with experiment. Thus, the isopropyl and *tert*-butyl compounds are found to be less stable than their primary isomers. The energy differences, of 0.82 and 5.21 kcal/mol, respectively, are of the correct order of magnitude considering that the *n*-propyl derivative is favored by 9 to 1 in the equilibrium, whereas the isobutyl compound is solely present at equilibrium.[3] In the case of the heteroatom-substituted groups, only the branched compound is present at equilibrium with the cyano substituent, whereas a 1:1 mixture is obtained with the trifluoromethyl group.[3] Here too, the computations are in full agreement with experiment, with the two $-CF_3$-substituted compounds predicted to be nearly isoenergetic and the $-CH(CH_3)$-CN compound lying as much as 6.65 kcal/mol below its isomer.

Interpreting the relative energies is less easy than in the case of the lithium and zirconium compounds. The main reason for this is illustrated by the charges in Table 4: the overall polarity of the metal−carbon bond is lower than in these previous examples, so that the electronegativity effect is smaller, and steric effects, which are harder to interpret, have a much larger relative role in determining the overall MSE. For example, the primary isobutyl compound is unexpectedly *less* stable than the secondary isopropyl one. Upon inspection of the geometries, this can be seen to be due to steric effects, with one of the β-methyl groups lying fairly close to the sulfur atom of the dithiocarbamato ligand. The alkyl group has also undergone a substantial rotation around the Pd−C bond so as to relieve this source of strain. The *tert*-butyl compound suffers from steric strain in a more obvious way. In this case, to minimize repulsion between one of the methyl groups and the phosphine, rotation around the Pd−C bond occurs, leaving another of the methyl groups rather close to the sulfur atom.

Turning to the heteroatom-substituted groups, it can be seen that an electron-withdrawing substituent in the β position has quite a strong *stabilizing* effect (compare the MSEs of *n*-propyl, $-CH_2CH_2CN$, and $-CH_2CH_2$-CF_3). This is presumably due to some hyperconjugative electronic stabilization of the partial negative charge at the α-carbon, as is suggested also by the fact that the overall negative charge on these groups is significantly larger than that found on the other primary alkyl groups. For the cyano substituent, this effect is even stronger in the branched isomer, where normal resonance can intervene to stabilize the partial negative charge. This leads to an even larger metal to alkyl charge transfer. On the basis of the charges alone, one might expect a similarly strong effect for the branched trifluoropropyl group. In fact, there almost certainly is a quite strong electronic contribution favoring the branched isomer in this case, too. However, it is offset here by a steric effect due to the much larger bulk of the CF_3 group (as compared, for example, to the cyano substituent). As in the *tert*-butyl compound, there is no ideal orientation for the alkyl group around the Pd−C group; in this case, there result fairly close interactions between the sulfur and the CF_3 and CH_3 groups, as well as between the CF_3 group and the methyl groups on the phosphine. The electronic stabilization still dominates, leading to the positive MSE, but this is quite small and barely larger than that of the linear compound.

In conclusion, due to the higher electronegativity of palladium(II), it forms less polar bonds to carbon, and the electronegativity effect favoring methyl and primary alkyl groups over secondary and tertiary ones is much smaller. The positions of the experimentally observed equilibria in these compounds result from a combination of this weak electronic effect and of steric effects, in

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[28] See e.g. Creve, S.; Oevering, H.; Coussens, B. B. *Organometallics* **1999**, *18*, 1967−1978.

[29] For a study of the stabilizing effect of electron-withdrawing α-nitrile groups on some different alkyl−palladium(II) compounds, see: Sakaki, S.; Biswas, B.; Sugimoto, M. *Organometallics* **1998**, *17*, 1278−1289.

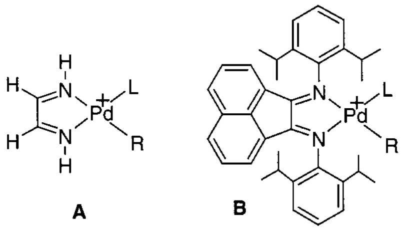

Figure 4. Small (A) and large (B) models of the diimino palladium(II) complexes. The external ligand L = nothing, C_2H_4, CH_3CN, $(CH_3)_2S$, or $(CH_3)_2O$.

which the neighboring sulfur atom of the dithiocarbamato ligand plays a previously unacknowledged role.

5. Diiminoalkyl Palladium(II) Cationic Complexes. This final class of compounds is of great interest due to their role, and that of the isoelectronic nickel analogues, in polymerization catalysis.[30] Due to this importance, both types of compounds have already been the object of a large number of computational studies, mostly focusing on the *mechanism* of the chain-propagation, branching, and termination steps.[15,31] As with the alkylzirconocene cations above, therefore, some of the data computed here are already available in previous work. The focus of the present work is on trying to rationalize the equilibria observed by Brookhart et al. for a set of propyl complexes bearing additional ethylene, acetonitrile, propene, or dimethyl sulfide ligands.[13] In a first step, the small model compounds shown as “A” in Figure 4 were used to derive MSEs and thereby predict the position of equilibria for the propyl complexes. Steric effects are minimal in this small system, so that the preference for primary versus secondary alkyl groups should reflect the intrinsic electronic properties of the $[\{\text{diimino}\}Pd(L)]^+$ system. Next, the calculations were repeated for the actual system present in the experimental equilibrium studies, shown as “B” in Figure 4, in which the bulky *o,o′*-(bisisopropyl)phenyl groups introduce very considerable steric effects.

The geometries obtained in this part of the study do not, for the most part, require commenting upon. The structure of the isopropyl derivative of the large system, with the dimethyl sulfide external ligand, is shown in Figure 5 as an example. To calibrate the accuracy of the method used, the geometry of the neutral complex shown in Figure 6 was also optimized at the same level of theory. Reasonable agreement on bond lengths and angles is found with the X-ray structure reported for the identical compound,[13] as also shown in Figure 6.

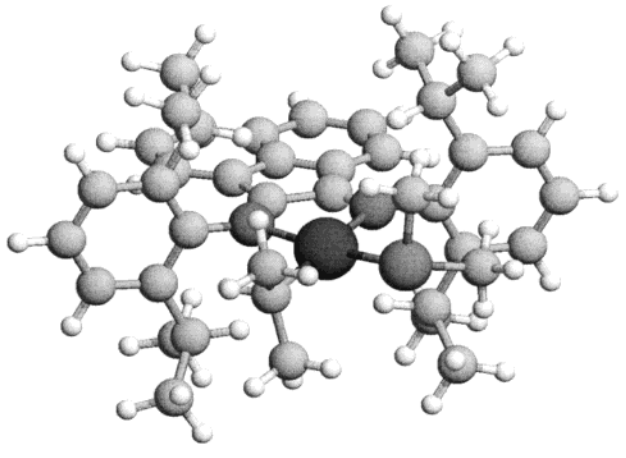

Figure 5. Optimized structure of the $[\{\mathbf{NN}\}Pd\{S(CH_3)_2\}CH(CH_3)_2]^+$ complex.

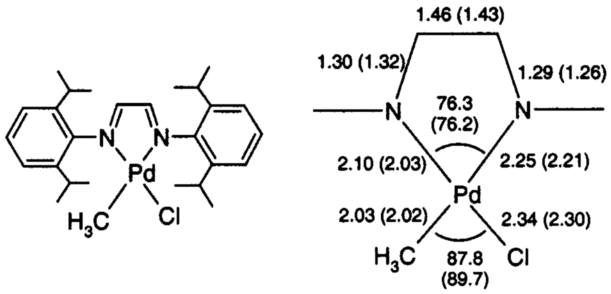

Figure 6. Selected computed and experimental[13] (values in brackets) bond lengths (Å) and angles (deg) of a Pd(II) diimino complex.

Table 5. Calculated Methyl Alkyl Transfer Stabilization Energies (MSEs, kcal/mol) of Alkyl Diiminopalladium Compounds $[\{\mathbf{NN}\}\mathbf{Pd(L)R}]^+$, Where {NN} Is the Diimino Ligand and L Is the Supplementary Ligand, and the NPA Total Charge on the Methyl Group in $[\{\mathbf{NN}\}\mathbf{Pd(L)CH_3}]^+$ Compounds, the Computed Δ*E*, and the Experimental Δ*G* Values between *n*-Propyl and Isopropyl Compounds

L/R	*n*-propyl	isopropyl	*Q*(Me)	$\Delta E_{n,i}$(comp)	$\Delta G_{n,i}$(exp)[a]
		“Small”, Model, System **A**			
/	18.14	20.07	−0.046	−1.93	/
C_2H_4	2.40	3.42	−0.068	−1.02	/
$(CH_3)_2O$	2.32	3.12	−0.091	−0.80	/
CH_3CN	1.93	2.37	−0.087	−0.44	/
$(CH_3)_2S$	1.53	1.68	−0.119	−0.15	/
Cl^-	1.03	0.87	−0.150	0.16	/
		“Large”, Real, System **B**			
/	12.65	14.36	−0.143	−1.71	−1.2
C_2H_4	0.00	−2.64	−0.109	2.64	1.2
$(CH_3)_2O$	0.41	−0.84	−0.165	1.25	/
CH_3CN	0.66	0.31	−0.125	0.35	−0.5
$(CH_3)_2S$	−1.04	−4.04	−0.163	3.00	2.0

[a] Ref 13.

The energetic data for these systems are summarized in Table 5. To start with the unhindered model A with no additional ligand (L = /), it can be seen that both the *n*-propyl and isopropyl systems are quite strongly stabilized with respect to the methyl derivative. This is due to a β-agostic interaction, which is stronger in these palladium compounds than in the zirconocenes discussed above because instead of involving only C−H $\sigma \rightarrow$ M (d) donation, there is back-donation from filled d orbitals on palladium into the C−H σ^* orbital. This also shows up in the geometries: the agostic C−H bond is considerably lengthened (e.g., $r_{C-H} = 1.22$ Å in the *n*-propyl complex). It can also be seen that the branched isomer is more stable in this case, by ca. 2 kcal/mol. This is because the electronegativity effect is *reversed* in these compounds, with branched isomers more stable. In turn, this is due to the fact that the palladium atom

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(30) It should be pointed out that the nickel complexes are actually better polymerization catalysts. However, the very careful equilibria study of ref 13 has only been carried out for the palladium derivatives.

(31) Selected references: (a) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177−6186. (b) Strömberg, S.; Zetterberg, K.; Siegbahn, P. E. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4147−4152. (c) Musaev, D. G.; Svensson, M.; Morokuma, K.; Strömberg, S.; Zetterberg, K.; Siegbahn, P. E. M. *Organometallics* **1997**, *16*, 1993−1945. (d) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581−1587. (f) Michalak, A.; Ziegler, T. *Organometallics* **1999**, *18*, 3998−4004.

in these compounds is less electron-releasing in its bonding to carbon, as shown by the overall NPA charge on the methyl group, which is essentially equal to zero and thereby much smaller than in the more electron-rich palladium compounds discussed in the previous section.

Turning now to the compounds including an external ligand bound to palladium, it can first of all be seen that all the corresponding MSEs are much smaller. This is due to the fact that there are now no stabilizing β-agostic interactions in the propyl complexes. That all the MSEs remain positive shows that the ligands do not alter the polarity of the Pd−C bond enough to reverse the trend favoring branched alkyl groups. However, the Pd−C bond does become slightly more ionic, roughly speaking increasingly so with increased donor character of the ligand, although the overall charge on methyl remains smaller than in the dithiocarbamato compound of the previous section. Also shown in Table 5 are the corresponding MSEs and charge for the neutral complex formed when the external ligand is a chloride anion. The charge on the methyl group is larger than in any of the cationic complexes, and the *n*-propyl compound is now very slightly more stable than the isopropyl one. Clearly, in these model compounds in which steric effects only play a minor role, one can observe an *indirect* electronic effect due to the donating properties of the external ligand. The more the ligand donates electrons to palladium, the more the Pd−C bond is polarized toward carbon, and the smaller the preference for branched alkyl groups. This effect is however much weaker than in the iron compounds discussed previously, presumably due to the intrinsically less ionic character of the Pd−C bond in these compounds, compared to the Fe−C bond.

The first thing to notice in the second part of Table 5, which shows the results for the larger, “real” system B, is that the predicted energy difference between the *n*-propyl and isopropyl compounds is in fair agreement with the experimental data for the corresponding ΔG of isomerization, derived from the measured equilibrium constants. With no additional ligand, the branched isomer is predicted to be more stable and is indeed found in the experiment to be present in ca. 20-fold excess over the linear isomer.[13] Adding a ligand leads to the linear isomer being more favored, with the ligands having progressively more effect in the order $CH_3CN < C_2H_4 < (CH_3)_2S$. Although the computed ΔE and experimental ΔG values are not identical, they follow the same order.

This order is however different from that found for the small, model systems, suggesting that steric effects swamp the smaller electronic effects which are alone present in the simpler model compounds. For the ligand-free system, the effect of the bulky side chains is to reduce substantially the MSEs for both *n*-propyl and isopropyl. However, the relative stability of the two isomers is not much affected, because these β-agostic complexes in fact have very similar geometries.[32] This is not at all true for the systems with an additional ligand, where there is no longer a β-agostic interaction, and the MSEs of the more hindered isopropyl complexes consequently drop much more than those of their linear isomers. In turn, this leads to a reversal in the relative stability of the isomers, with the *n*-propyl complexes becoming more stable in all cases. The electron-donating properties of the ligands may make a small contribution to this reversal, but the main cause is clearly steric effects. For example, the strongest destabilization occurs in the dimethyl sulfide/isopropyl complex, and inspection of the structure (see Figure 5) clearly reveals the hindered nature of this species, with the S-methyl groups interacting unfavorably with the isopropyl chains on the *N*-phenyl substituents.

It can also be noted that the NPA charges on the methyl group no longer follow a rational order as in the model complexes. This may indicate that the geometrical constraints imposed by the steric effects lead to changes in the nature of the bonding as well.

In summary, these diimino palladium complexes reveal an interesting interplay between electronic and steric effects in determining the relative stability of primary and secondary alkyl groups. The intrinsic electronic properties of the palladium atom in this system favor the branched isomer, in contrast to all the other metal complexes discussed above, where primary isomers are favored. This reversal is due to the fact that the Pd−C bond in these complexes has barely any ionic character. As shown experimentally,[13] primary complexes only become predominant in these complexes in the presence of a very bulky diimino ligand, and, even more important, an additional, “external”, ligand. The key role played by this fourth ligand has also been highlighted in a previous computational study.[15] However, the electronic effect demonstrated here in the case of the unhindered model of these complexes probably plays some role in affecting the equilibria in the real, bulky system. This suggests that further modification of the diimino ligand to make it more electron-donating (e.g., by using *p*-methoxy phenyl groups on the nitrogen atoms) would favor linear isomers still more, thus leading to a greater degree of chain-straightening in polymerization catalysis.

Conclusions

This survey of a very broad range of transition metal alkyl complexes has shown that electronic effects indisputably play a much larger role than is generally acknowledged in determining the general preference for primary over secondary or tertiary isomers. This is because metal−carbon bonding is often substantially ionic in nature, with a large negative charge on the alkyl group and because primary carbanions are more stable than secondary or tertiary ones. In fact, steric effects, which are very commonly used in the literature to explain the preference for primary groups, appear to play only a minor role in many of the compounds studied here. Exceptions do of course occur, for example with very bulky alkyl groups (e.g., *tert*-butyl), or with very bulky ligands (e.g., the Cp*$_2$Zr or “large” diimino-Pd

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(32) This conclusion is slightly at variance with that in ref 15, in which results similar to ours are obtained using the BP86 functional for the same “small” and “large” versions of these palladium *n*- and isopropyl complexes. In that study, the difference in energy favoring the isopropyl isomer is found to be slightly larger in the large system than in the small one (2.65 vs 1.96 kcal/mol), and the authors attribute this to steric effects. In any case, the small energy changes involved are not relevant here.

systems). Another case where steric rather than electronic effects tend to dominate is when the properties of the metal (oxidation state, ancillary ligands) are such that the metal−carbon bond is not highly ionic. This situation, which occurs in the present study for all the palladium compounds, leads to the intrinsic electronic preference for primary isomers being small, or indeed to a reversed preference for branched isomers. Either way, steric effects will then tend to dominate except in the most unhindered situations.

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Supporting Information Available: Optimized structures of all the species discussed in the text (Cartesian coordinates, in Å) and total electronic energies for all these species. This material is available free of charge via the Internet at http://pubs.acs.org.

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