

Why Does the Tetrakis(trimethylphosphine)iridium(III) Hydridochloride Cation Adopt the Sterically and Electronically Unfavorable *Cis* Geometry?

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Although the tetrakis(trimethylphosphine)iridium(III) hydridochloride cation, $[\text{HIrCl}(\text{PMe}_3)_4]^+$, and similar complexes would intuitively be expected to adopt a *trans* geometry on electronic and sterical grounds, experimentally the *cis* geometry is found to prevail. Quantum chemical calculations suggest that the *trans* and *cis* structures are nearly isoenergetic, such that the *cis:trans* equilibrium is dominated by the higher entropy of the lower symmetry *cis* structure.

Introduction

The relative stability of geometrical isomers plays a major role in determining the course and outcome of many organometallic reactions, because the intermediates are often coordinatively unsaturated and capable of facile isomerization. Hence, controlling these isomerizations is at the heart of the design of stereospecific or enantioselective catalysis. It is currently believed that ligand effects, both steric and electronic, are the dominant nonenvironmental factors that determine the relative stabilities of coordination compound isomers.¹ Here we demonstrate that neither steric nor electronic arguments can predict correctly the stable isomer of the octahedral RML_4 complexes (R = strong σ -donor such as hydride, methyl, and phenyl; M = Ir(III), Ru(II), and Os(II); X = weak σ -donor such as halide, OR, SH, NHR, PHR, H_2O , NH_3 , CO, CH_3CN , and $\eta^2\text{-H}_2$; L = PMe_3 and $\text{PMe}_2(\text{C}_6\text{H}_5)$). Of the two possible isomers of RML_4 (**1**, **2**), the *trans* configuration is predicted to be *sterically* more stable, because each of the largest ligands (L) has only two large neighbors at 90° positions, whereas in the *cis* isomer, two of the L groups have three large neighbors *cis* disposed. *Electronic* considerations also suggest that the *trans* R-M-X geometry should be the most stable, since the R group is the best σ -donor (thus, having the largest *trans* influence),² and since X is the weakest σ -donor. Nevertheless, we observed the *trans* to *cis* isomerization of $[\text{HIrCl}(\text{PMe}_3)_4]^+$, indicating that contrary to electronic and steric arguments, the *cis* isomer is thermodynamically more stable. We observed a similar *trans* to *cis* isomerization during the oxidative addition of water, methanol, and H_2S to $[\text{Ir}(\text{PMe}_3)_4]\text{PF}_6$, but were unable to isolate the *trans* products.^{3,4} Our

quantum mechanical calculations suggest that entropy contributions originating in different symmetries dominate the equilibrium between the isomers.

Experimental and Computational Details

All syntheses and chemical manipulations were carried out under nitrogen in a Vacuum Atmospheres DC-882 glovebox. All solvents were reagent grade or better. THF was prepurified through a column of basic alumina. Both THF and pyridine were refluxed over Na/benzophenone ketyl, distilled under argon and stored over activated 4 Å molecular sieves. All deuterated solvents were purchased from Aldrich, degassed and dried over a large amount of 3 Å molecular sieves for at least one week before use. ^1H and ^{31}P NMR spectra were recorded at 400.19 and 161.9 MHz, respectively, using a Bruker AMX 400 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si and referenced to the residual solvent- h_1 or downfield from external H_3PO_4 85% in D_2O .

Preparation of *trans*- $[\text{HIrCl}(\text{PMe}_3)_4][\text{OSO}_2\text{-}p\text{-tolyl}]$ (1**).** *p*-Toluenesulfonic acid monohydrate (14 mg, 7.36×10^{-2} mmol) dissolved in dry THF (2 mL) was added to a suspension of the previously reported⁵ $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ (41 mg, 7.71×10^{-2} mmol) in THF (4 mL) at room temperature. The red solid turned white during 5 min, and the solution became colorless. After 30 min the solid was isolated by filtration, yielding **1** as the single product. ^1H NMR (pyridine- d_5): 8.51 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, *ortho* to IrOSO_2), 7.12 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 2H, *ortho* to CH_3), 1.69 (t, $^{\text{virtual}}J_{\text{H-P}} = 3.1$ Hz, 36H, $4\text{P}(\text{CH}_3)_3$), -21.74 (quintet, $^2J_{\text{H-P}} = 14.6$ Hz, 1H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (pyridine- d_5): -45.6 (s). IR (Nujol): 2163 (strong, $\nu_{\text{Ir-H trans}}$ to a weak σ -donor). Anal. Calcd: C 33.90, H 6.59. Found: C 33.77, H 6.42.

Preparation of *cis*- $[\text{HIrCl}(\text{PMe}_3)_4]\text{PF}_6$ (2**).** Bubbling dry gaseous HCl (99.999% purity) through a red THF (10 mL) solution of $[\text{Ir}(\text{PMe}_3)_4]\text{PF}_6$ (**6**) (51 mg) for 2 h caused bleaching. The solvents were stripped off under high vacuum, yielding complex **2** as a white solid. ^1H NMR (pyridine- d_5): 1.80 (d, $^2J_{\text{H-P}} = 10.3$ Hz, 9H, $\text{P}(\text{CH}_3)_3$ *trans* to Cl), 1.74 (t, $^{\text{virtual}}J_{\text{H-P}} = 3.8$ Hz, 18H, $2\text{P}(\text{CH}_3)_3$ mutually *trans*), 1.54 (dd, $^2J_{\text{H-P}} = 8.2$ Hz, $^4J_{\text{H-H,trans}} = 1.0$ Hz, 9H, $\text{P}(\text{CH}_3)_3$ *trans* to H), -11.65 (dtd (apparent dq), $^2J_{\text{H-P,trans}} = 148.3$ Hz, the weighed average of

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$^2J_{\text{H-P, cis}}$ and $^2J_{\text{H-P, cis}} = 18.7$ Hz, 1H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (pyridine- d_5): -45.7 (dt, $^2J_{\text{P-P, cis}} = 18.0$ Hz, $^2J_{\text{P-P, cis}} = 11.5$ Hz, 1P *trans* to H), -47.5 (dd (apparent t), the weighed average of $^2J_{\text{P-P, cis}}$ and $^2J_{\text{P-P, cis}} = 19.0$ Hz, 2P mutually *trans*), -54.1 (td, $^2J_{\text{P-P, cis}} = 20.2$ Hz, $^2J_{\text{P-P, cis}} = 11.3$ Hz, 1P *trans* to Cl), -142.0 (heptet, $^1J_{\text{heptet P-F}} = 710$ Hz, 1P). IR (Nujol): 2065 (strong, $\nu_{\text{Ir-H trans}}$ to a strong σ -donor). Anal. Calcd: C 22.28, H 5.76. Found: C 22.01, H 5.57.

Isomerization of *trans*- $[\text{HIrCl}(\text{PMe}_3)_4][\text{OSO}_2\text{-}p\text{-tolyl}]$ (1) to the *cis* Isomer 2. (a) At room temperature, in a pyridine- d_5 solution: The isomerization is very slow, and does not reach equilibrium within a week. (b) At 65 °C: A THF solution of 1 in a sealed bottle was kept in an oil bath at 65 °C for 48 h. The bottle was quickly cooled to -78 °C and allowed to warm slowly to room temperature. The solvent was stripped off under vacuum, and the white residue was redissolved in pyridine- d_5 . The 1:2 ratio obtained was 1:6.

Computational Methods. All the calculations were carried out on DEC Alpha 500/500 and SGI Octane workstations using Gaussian 98.⁷

The Hay-Wadt Los Alamos National Laboratory 2-shell double- ζ (LANL2DZ) basis set/relativistic effective core potential (RECP) combination⁸ was used for the geometry optimizations and for the harmonic frequency calculations involved in the zero-point vibrational energies (ZPVE) and in setting up the partition functions for the rigid rotor-harmonic oscillator (RRHO) thermal corrections. As is customary, the Dunning valence double- ζ basis set⁹ was used on hydrogen and first-row atoms.

The relative energies of the different structures were in addition evaluated with the same basis set-RECP combination, augmented with polarization functions taken from ref 10; this is denoted by the acronym LANL2DZP throughout the paper. (For hydrogen and first-row atoms, the Dunning cc-pVDZ basis set¹¹ was used in this case.) Tightened convergence criteria were used throughout for the SCF/Kohn-Sham iterations and where possible for the geometry optimizations.

To ensure reproducibility of energies, geometries, and computed thermodynamic functions to the precision tabulated, it was found necessary to use finer DFT integration grids than the Gaussian 98 defaults. For all energy and gradient steps, we employed a pruned (99,590) grid (i.e., a 590-point Lebedev angular grid¹² combined with a 99-point Euler-Maclaurin radial grid¹³) rather than the (75,302) default, while the pruned (50,194) SG1 grid¹⁴ (rather than the (35,110) default) was used in solving the coupled perturbed Kohn-Sham equations. For third-row transition metal compounds, the errors incurred in

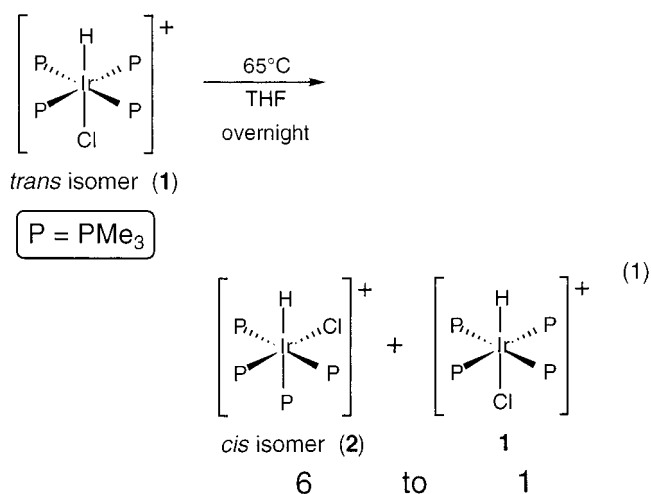
the total energies by the use of the default grids are several orders of magnitude larger than those incurred by using the default energy convergence criteria.¹⁵

We used a number of exchange-correlation (XC) functionals: (1) local density approximation (LDA);^{16,17} (2) the gradient-corrected Becke-Lee-Yang-Parr (BLYP) functional (the Becke 1988 exchange functional¹⁸ with Lee-Yang-Parr (LYP) correlation;¹⁹) (3) the popular Becke 3-parameter-Lee-Yang-Parr (B3LYP) functional (Becke's 3-parameter hybrid exchange functional²⁰ with LYP correlation); (4) the mPW1PW91 functional recently proposed by Adamo and Barone²¹ (a 1:3 mixture²² of Hartree-Fock and modified Perdew-Wang 1991 exchange²³ with standard Perdew-Wang 1991 correlation²³). The latter appears to yield a better description of long-range interactions than standard XC functionals.^{21,24}

In addition, we carried out Hartree-Fock calculations for comparison; these could be considered a special case of hybrid DFT functionals, with 100% Hartree-Fock exchange and no correlation. All relevant results can be found in Table 1.

Results and Discussion

trans- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ (1) is obtained within minutes as a pure white solid by protonation of the previously reported⁵ $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ suspended in THF with an equimolar amount of *p*-toluenesulfonic acid. Heating of 1 at 65 °C in THF overnight yields a 6:1 mixture of *cis*- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ (2) and *trans*-1 (eq 1). Isomerization of 1 to 2 takes place also in pyridine- d_5 at room temperature, albeit slowly. Complex 2 can be prepared directly from the previously reported⁶ $[\text{Ir}(\text{PMe}_3)_4]\text{PF}_6$ by bubbling gaseous HCl through its red THF solution.



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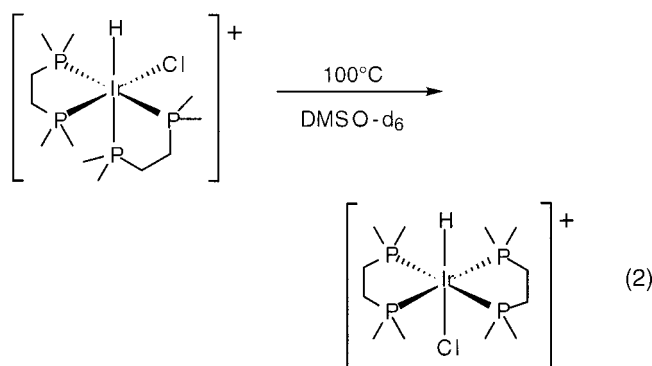
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Table 1. *Cis–trans* Energy Difference (kcal/mol) for Various [HIrClL₄]⁺ Complexes^a

	4 PH ₃	4 PMe ₃	2 H ₂ PCH ₂ CH ₂ PH ₂	2 Me ₂ PCH ₂ CH ₂ PMe ₂
		ΔE_e , LANL2DZ		
HF	2.36	0.98	9.17	11.87
mPW1PW91	1.11	1.04	7.34	9.94
LDA	1.07	3.31	6.84	9.24
BLYP	−0.19	−0.16	5.90	8.46
B3LYP	0.60	0.68	6.84	9.47
		ΔE_e , LANL2DZP		
HF	1.96	0.64	8.88	11.71
mPW1PW91	0.56	0.88	7.01	9.68
LDA	0.28	3.09	6.42	8.82
BLYP	−0.57	−0.78	5.75	8.35
B3LYP	0.21	0.17	6.67	9.30
Zero-Point Vibration and Temperature Effects (B3LYP/LANL2DZ)				
$\Delta ZPVE$	−0.18	−0.04	−0.17	−0.21
$\Delta(H_{298} - H_0)$	−0.06	−0.14	−0.02	+0.02
ΔS_{rot} (incl. $R \ln 2$)	2.80	1.40	1.44	1.39
ΔS_{vib}	−3.23	1.04	−0.95	0.33
ΔS_{total}	−0.43	2.44	0.49	1.72
$\Delta(G_{298} - H_{298}) = -T\Delta S_{298}$	+0.13	−0.73	−0.15	−0.51
		ΔG_{298} (LANL2DZP) ^b		
HF	1.85	−0.26	8.55	11.00
mPW1PW91	0.44	−0.01	6.67	8.97
LDA	0.17	2.19	6.08	8.10
BLYP	−0.68	−1.67	5.41	7.64
B3LYP	+0.10	−0.73	6.33	8.59

^a A negative sign implies the *cis* form to be more stable. ^b $\Delta E_e[\text{LANL2DZP}] + \Delta ZPVE[\text{B3LYP/LANL2DZ}] + \Delta(G_{298} - H_0)[\text{B3LYP/LANL2DZ}]$.

Replacing the four PMe₃ ligands by two chelates of the closely analogous 1,2-bis(dimethylphosphinoethane) (DMPE) reverses the stability order of the isomers. Behr and co-workers reported that heating *cis*-[HrCl(DMPE)₂]⁺ to 100 °C in DMSO yields the *trans* isomer as the single product (eq 2).²⁵



The unusual stability of *cis*-RMX(PMe₃)₄ is not unique to iridium. A large series of analogous d⁶ ruthenium complexes exhibits the same phenomenon:²⁶ R = hydride, X = OH,²⁷ *p*-OC₆H₄CH₃,²⁸ *p*-OC₆H₄(OCH₃),²⁹ *p*-OC₆H₄Cl,³⁰ *p*-OC₆H₄NO₂,³⁰ N(H)C₆H₅,²⁸ P(H)C₆H₅,³⁰ *p*-SC₆H₄(CH₃),³⁰ Cl,^{31,32} and NH₃,³³ R = phenyl, X =

OH,³⁴ OCH(CH₃)₂,³⁴ *p*-OC₆H₄(CH₃),³⁴ OC(=CH₂)C₆H₅,^{34,35} oxygen-bound enolates,³⁵ and N(H)C₆H₅.³⁴ R = methyl, X = OH,³⁵ and Cl.³² *cis*-HO(OH)(PMe₃)₄ probably belongs to this family of complexes as well.³⁶ *Cis* to *trans* isomerization at room temperature was reported also with another phosphine (L = PMe₂(C₆H₅), R = hydride, X = η²-H₂).³⁷ Replacing PMe₃ by DMPE reverses the relative stabilities of the isomers for the ruthenium complexes as well (R = hydride, X = OH,³⁵ OC(O)H,³⁸ OC(O)C₆H₅,³⁹ and Cl⁴⁰). For none of these ruthenium complexes did the authors consider the stability issue addressed here.

In addition to the electronic (mainly σ-donation by the ligands) and steric factors, the π-donation capability of the weak σ-donor is unimportant in reversing the expected stability order of RMX(PMe₃)₄, since X can also be NH₃,³³ η²-H₂,³⁷ CH₃CN,³³ or CO³³ (not π-donors).

Quantum Chemical Calculations. To explain the unexpected stability order of the [HrCl(PMe₃)₄]⁺ isomers, we have calculated the energy differences between the *cis* and the *trans* configurations of various [Hr-

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$\text{CIL}_4]^+$ complexes using a variety of quantum chemical approaches. All relevant results are reported in Table 1.

At the B3LYP/LANL2DZ level, *trans*- $[\text{HIrCl}(\text{PH}_3)_4]^+$ is found to have a 4-fold symmetry axis (point group C_{4v}), while the corresponding *cis* structure only has a symmetry plane (point group C_s). Upon introducing the methyl groups on the phosphines, the symmetry of the *trans* isomer drops to C_{2v} , while *cis*- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ has no symmetry at all. At the HF/LANL2DZ level, *trans*- $[\text{HIrCl}(\text{PH}_3)_4]^+$ is found to be 2.4 kcal/mol more stable than its *cis* counterpart; upon introducing the Me groups, the difference is reduced to 1.0 kcal/mol. Enlargement of the basis set shifts the equilibrium toward the *cis* structures, as it does in the various DFT calculations.

At the B3LYP level, *trans*- $[\text{HIrCl}(\text{PH}_3)_4]^+$ and *trans*- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ are found to be 0.6 and 0.7 kcal/mol more stable than their respective *cis* counterparts. Enlargement of the basis set largely eliminates these differences, leading to the isomers being nearly isoenergetic. The difference between the HF and B3LYP results is probably mainly due to correlation effects, since the exchange behavior of HF and B3LYP is expected to be similar by design.

LDA exhibits a pronounced shift of the equilibrium toward the *trans* form upon Me substitution (ΔE changing from 1.07 to 3.31 kcal/mol with the LANL2DZ and from 0.28 to 3.09 kcal/mol with the LANL2DZP basis set), which is quite absent in the gradient-corrected and hybrid functionals; we conclude that LDA is inadequate even for this comparatively simple problem. By comparing LDA to BLYP results, we find that the gradient corrections cause fundamental changes; as expected, the B3LYP results (relative to BLYP) move slightly in the direction of the HF values because of the admixture of HF exchange. We note that trends in the mPW1PW91 results appear to parallel those at the B3LYP level, although the former exchange–correlation functional tends to favor the *trans* form relative to B3LYP. Overall, we see a sequence $\text{HF} \approx \text{mPW1PW91} > \text{B3LYP} > \text{BLYP}$ for the relative energy.

In light of the smallness of the energy changes involved, it would have been desirable to carry out all optimization at the B3LYP/LANL2DZP level as well. However, considering that the B3LYP/LANL2DZ optimization on the largest system required about 2 months CPU-time-equivalent on an SGI Origin 2000, this does not appear to be a realistic option at present.

Introduction of zero-point energy slightly favors *cis* over *trans*- $[\text{HIrCl}(\text{PH}_3)_4]^+$, but has essentially no effect for $[\text{HIrCl}(\text{PMe}_3)_4]^+$. Introduction of the enthalpy functions $H_{298} - H_0$ has essentially no effect for *trans*- versus *cis*- $[\text{HIrCl}(\text{PH}_3)_4]^+$, but slightly favors *cis* over *trans* once the Me groups are introduced, although this small effect is within the error margin of the calculation.

What is the effect of entropy on the equilibrium? Entropy contributions to steric interaction are expected to favor the *trans* isomer,⁴¹ in contradiction with the observed relative stabilities. Within the RRHO approximation, the entropy contribution to the equilibrium consists of three terms:

(a) The first term is the rotational symmetry contribution $R \ln(\sigma_{\text{trans}}/\sigma_{\text{cis}})$, where σ_{cis} and σ_{trans} are the rotational symmetry numbers of the *cis* and *trans* isomers, respectively. In the case of $[\text{HIrCl}(\text{PH}_3)_4]^+$, $\sigma_{\text{cis}} = 2$ (symmetry C_s) and $\sigma_{\text{trans}} = 4$ (symmetry C_{4v}), while for $[\text{HIrCl}(\text{PMe}_3)_4]^+$ (1 vs 2), $\sigma_{\text{cis}} = 1$ (symmetry C_1) and $\sigma_{\text{trans}} = 2$ (symmetry C_{2v}). Either case leads to a contribution to ΔS of $R \ln 2$ (1.4 eu), and hence of $-RT \ln 2$ to ΔG (0.41 kcal/mol at room temperature). This would translate into a 2:1 equilibrium in favor of the *cis* isomer in an otherwise fully thermoneutral system. The same applies to the phosphochelate systems, where the *trans* and *cis* isomers have C_2 and C_1 symmetry, respectively. (Quantum chemical packages with integrated RRHO features such as Gaussian 98 will only include this term correctly if the correct molecular symmetry is imposed.)

(b) The second is a rotational entropy term, which from standard statistical thermodynamics is found to be $(R/2) [\ln I_{A,\text{cis}} I_{B,\text{cis}} I_{C,\text{cis}} - \ln I_{A,\text{trans}} I_{B,\text{trans}} I_{C,\text{trans}}]$, in which I_A , I_B , and I_C represent the three molecular principal moments of inertia. Since in the $R = \text{H}$ case the *trans* isomer (an oblate symmetric top) is appreciably more “compact” than the *cis* isomer in terms of having a smaller $I_A I_B I_C$ product, its rotational entropy is decreased by an additional 1.4 eu. For the bulkier $R = \text{Me}$ and phosphochelate cases, this particular difference is not significant enough to be reflected in the entropy.

(c) The lower symmetry structures are expected to be less rigid and hence to have, on average, more low-lying vibrational levels. This effect contributes about 1 eu in the $R = \text{Me}$ case; given the limitations of the RRHO approximation for systems with many low-barrier hindered rotors, this contribution is at best semiquantitative, however. (While most of the error thus incurred should cancel between the two isomers, complete cancellation should not be taken for granted.) In the $R = \text{H}$ case, a contribution of -3.2 eu in the opposite direction is surprisingly seen. Upon close inspection, this is found to be due mostly to an anomalously low frequency for concerted PH_3 rotation.

The bottom line of the above considerations is that even if the *cis*- and *trans*- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ structures were perfectly isoenergetic at 0 K, entropy effects would slightly favor the *cis* structure.

The 6:1 *cis:trans*- $[\text{HIrCl}(\text{PMe}_3)_4]^+$ ratio found experimentally—if we were to assume that no differential solvent effects exist between the structures—corresponds to a Gibbs energy difference of -1.15 kcal/mol at 298 K. This is in fact intermediate between the large basis set computed B3LYP (-0.73 kcal/mol) and BLYP (-1.67 kcal/mol) results: From the observed ΔG and the computed thermal corrections (keeping in mind the limitations of the RRHO approximation), we obtain a bottom-of-the-well energy difference of only about -0.4 kcal/mol favoring the *cis* form. We also note that the trend in the computed results suggests that basis set extension favors the *cis* form, and we expect this trend to be continued with further basis set enlargement.

It should be stressed that the basis sets employed are still quite some distance removed from the basis set limit, even for DFT methods, for which basis set convergence on a variety of properties is much faster

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Table 2. Metal–Ligand Bond Distances (Å) at the B3LYP/LANL2DZ Level

	<i>trans</i>			
	C_{4v} , 4 PH ₃	C_{2v} , 4 PMe ₃	C_{2h} , 2 H ₂ PCH ₂ CH ₂ PH ₂	C_{2h} , 2 Me ₂ PCH ₂ CH ₂ PMe ₂
H	1.596	1.600	1.596	1.596
Cl	2.544	2.576	2.552	2.568
P ₁	2.405	2.442	2.390	2.408
P ₂	2.405	2.459	2.392	2.412
P ₃	2.405	2.442	2.390	2.408
P ₄	2.405	2.459	2.392	2.412

	<i>cis</i>			
	C_s , 4 PH ₃	C_1 , 4 PMe ₃	C_1 , 2 H ₂ PCH ₂ CH ₂ PH ₂	C_1 , 2 Me ₂ PCH ₂ CH ₂ PMe ₂
H	1.598	1.599	1.602	1.607
Cl	2.471	2.515	2.479	2.500
P(trans H)	2.519	2.545	2.500	2.521
P(trans Cl)	2.378	2.389	2.363	2.339
P ₃	2.402	2.457	2.382	2.368
P ₄	2.402	2.462	2.391	2.414

than for conventional electron correlation methods.²⁴ Yet because we are merely comparing energies of two isomers with like connectivity (same number of bonds of each formal type) rather than considering the energy change of a reaction involving bond breaking, considerable error cancellation occurs, resulting in the surprisingly good agreement with experiment seen here.

What is the situation for the chelated complex [HrCl-(Me₂PCH₂CH₂PMe₂)₂]⁺? There too, entropy effects favor the *cis* form, but since ΔE_e favors the *trans* form and is an order of magnitude larger than $T\Delta S$ in this case, essentially 100% *trans* product is expected (and obtained). The addition of Me groups increases ΔE_e , as expected, at all levels of theory considered. The most notable trend among the levels of theory is that Hartree–Fock—relative to the various DFT exchange–correlation functionals—appears to be biased toward the *trans* form by 2–3 kcal/mol. It is well known that neglect of electron correlation usually results in overestimation of charge separation (expressing itself, among other things, in overestimated dipole moments and overly localized structures). Hence introduction of electron correlation would be expected to reduce the σ -donor effect of the substituents, which is consistent with the difference between Hartree–Fock and the various DFT results.

A similar trend is seen for the unchelated systems; however, both ΔE_e and the changes involved in it are smaller by almost an order of magnitude there. Why the difference? The computed metal–ligand bond distances (Table 2) offer a beginning of an explanation. As expected, in all *cis* cases the Ir–P bond *trans* to the Cl is shortened and that *trans* to the H is lengthened. (This trend is also reflected in the computed Wiberg bond orders⁴² from a natural population analysis.⁴³) However,

it is immediately seen that the geometry perturbation relative to the *trans* isomer is substantially larger in the chelated cases than in the unchelated ones; Me substitution further enhances the difference. (The P–Ir–P angles in the chelated complexes are all in the 85–87° range, close to the “bite angle” for the phosphochelate ligands.) This would suggest that the geometric constraints imposed by the chelate would be responsible for the different behavior of chelated and unchelated systems.

Summarizing, the computed results, theory, and experiment are fundamentally in agreement about the question at hand.

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Supporting Information Available: Computed (B3LYP/LANL2DZ) geometries in Xmol (.xyz) format, harmonic frequencies, and infrared intensities for the species in Table 1 are available in machine-readable form on the World Wide Web at the location <http://theochem.weizmann.ac.il/web/papers/isom.html>. The geometries can be visualized directly in any Xmol-compatible molecular viewer. This material is also available free of charge via the Internet at <http://pubs.acs.org>.

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