A Computational Study of the Effectiveness of the Frontier Molecular Orbital Formalism in Predicting Conformational Isomerism in (*p*-RC$_6$H$_4$NC)$_2$W(dppe)$_2$

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Ab initio electronic structure calculations on a series of ligands, *p*-RC$_6$H$_4$NC:, indicate that the energy of the LUMO correlates with the electron-withdrawing/donating capabilities of the substituent group, which determines the relative π-acidity of the ligand. Depending on the nature of the para substituent group on the aryl isocyanide ligand, bis(aryl isocyanide) complexes of tungsten-containing bulky bidentate arylphosphine ligands adopt either cis or trans conformations. The frontier molecular orbital formalism predicts that strong π-acids, which contain electron-withdrawing groups, tend to polarize sufficient charge density away from the metal center to effect the formation of the sterically less favorable but electronically stabilized cis conformer. Density functional theory calculations on similar complexes containing phosphines which do not impose severe steric contraints indicate that the balance between steric and electronic stabilization can be effectively predicted by comparing the relative energies of the ligand LUMOs.

INTRODUCTION

The frontier molecular orbital (FMO) formalism, first formulated for organic systems by Fukui,[1] has in more recent times been employed by transition-metal chemists as a qualitative tool to predict the reactivity and product geometry of organometallic molecules. The model is based on a "donor−acceptor" concept and considers the overlap between donor−acceptor orbitals and their relative energies. In the general case, for this model the strength of the donor−acceptor interaction is determined by the overlap between the HOMO of the donor and the LUMO of the acceptor (the more overlap the stronger the interaction) and the energy difference between the HOMO of the donor and the LUMO of the acceptor (the smaller the difference in energy the stronger the interaction). For organometallic complexes containing π-acids, the donor HOMO consists chiefly of occupied d orbitals on the metal, whereas the LUMO resides on the ligand; the resulting bonding scheme is traditionally described as "metal-to-ligand back-bonding".

Experimental work in our laboratories (D.W.B.) has been directed toward the creation of insulated, molecular-level wires in which electron-rich metal atoms (such as zerovalent tungsten) are bridged with conducting diisocyanide ligands[2] and surrounded by bulky organophosphine groups (dppe, 1,2-bis(diphenylphosphino)ethane):

In the course of this work we discovered that the monomeric species (*p*-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ tended to adopt a cis conformation that was not optimal for the formation of long-chain molecules capable of transporting charge (Figure 1a).[3] Furthermore, the isocyanide ligands
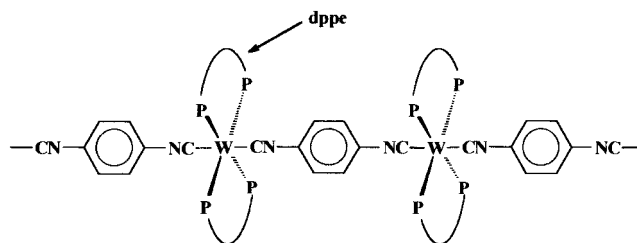
suffered extraordinary distortions in a sterically crowded environment, implying that the electronic stabilization was significant, overcoming relatively large steric repulsion, since the trans geometry would clearly be sterically favored. It was also observed that replacement of the strongly electron-withdrawing terminal CN group with an electron-donating methyl group resulted in the trans geometry for the resulting (*p*-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ complex (Figure 1b). In this case, the electronic stabilization was apparently not sufficient to overcome steric repulsions in the presence of the large, bulky phosphine groups surrounding the metal center.

The electronic stabilization of these complexes arises largely from the ability of π-acidic ligands to polarize charge away from the zerovalent metal center, a concept addressed directly by the FMO formalism. Thus, we postulated that the electron-withdrawing *p*-CNC$_6$H$_4$NC: ligand polarizes substantial charge out of the metal HOMO into a ligand LUMO which is relatively low in energy, preferring the cis conformation, which places each π-acidic ligand opposite an electron-donating phosphine. The more weakly π-acidic H$_3$CC$_6$H$_4$NC: ligand, with a higher ligand LUMO, would not effect enough stabilization energy to overcome steric repulsions, resulting in a trans conformation. In this paper we report the results of a computational and experimental test of this hypothesis.

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Table 1. Summary of Spectroscopic and Crystallographic Evidence for Conformational Assignment of *cis-* and *trans-*(p-RC$_6$H$_n$(CH$_3$)$_{4-n}$NC)$_2$W(dppe)$_2$

isocyanide ligand	assigned config	^{31}P chemical shift (ppm)[a]	ν_{CN} (coordinated)[b]	crystallogr
p-O$_2$NC$_6$H$_4$NC:	cis	30.8	1743 m	
		47.5	1662 m	
p-CNC$_6$H$_4$NC:	cis	32.1	1761 m	cis
		47.5	1662 m	
p-CNC$_6$H$_2$(CH$_3$)$_2$NC:	cis	32.0	1772 m	cis
		46.2	1669 m	
p-F$_3$CC$_6$H$_4$NC:	cis	32.2	1834 m	cis
		47.7	1693 m	
p-CNC$_6$(CH$_3$)$_4$NC:	trans	45.5	1943 w	
			1819 s, br	
p-FC$_6$H$_4$NC:	trans	51.0	1970 w	trans
			1865 s, br	
p-H$_3$CC$_6$H$_4$NC:	trans	47.9	1952 w	trans
			1873 s, br	
p-H$_3$COC$_6$H$_4$NC:	trans	47.2	1951 w	trans
			1822 s, br	

[a] Relative to 85% H$_3$PO$_4$ (0.0 ppm); ^{31}P NMR spectra acquired in THF. [b] KBr pellets; m = medium, s = strong, br = broad, w = weak, sym = symmetric, asym = asymmetric.
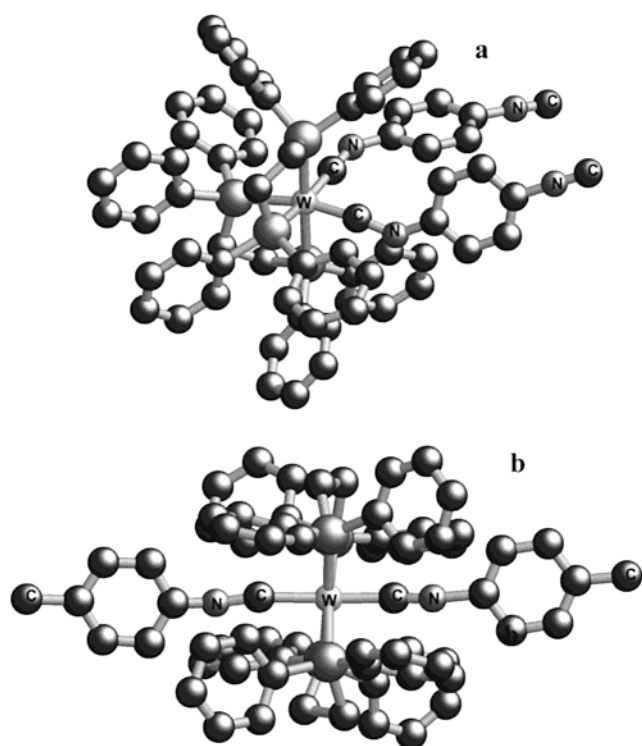
Figure 1. Structures of (a) *cis-*(p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ and (b) *trans-*(p-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$, determined by X-ray crystallography. Hydrogen atoms have been omitted for clarity.

COMPUTATIONAL METHODS

Ab initio restricted Hartree−Fock (RHF) calculations were performed on the ligands using the Gaussian 92[4] and Gaussian 98[5] programs. The basis sets used were STO-3G,[6,7] 6-31G,[8−10] and 6-31G**.[11,12] Ligands were geometry optimized via the Berny algorithm.[13] Parameters optimized included d_{C-N}, $d_{N\equiv C}$, and corresponding para substituent (C−R) bond lengths. The remaining molecular parameters were constrained to idealized geometries. Density functional calculations were performed with the density functional theory[14] (DFT) program DGauss.[15] The DZVP2 basis set[16] was used for all atoms except for tungsten. The Hay−Wadt effective core potential (ECP) and basis sets were used[17] with

the fitting sets in UniChem for the tungsten atom.[18] All calculations were performed at the local level with the potential fit of Vosko, Wilk, and Nusair.[19] The geometries were optimized by using analytic gradient methods; second derivatives were also calculated analytically.[20] We have shown in a number of publications that the LDFT level is appropriate for such studies.[21]

RESULTS AND DISCUSSION

This study was based on the premise that, for a given zerovalent transition-metal center, the electronic stabilization of complexes containing π-acids depends primarily on the energy of the LUMO of the ligand, and that sterically unfavorable geometries will occur only when that stabilization is sufficient to overcome steric repulsions. To test this hypothesis, a series of tungsten(0) bisisocyanide complexes containing bulky bidentate arylphosphine ligands were investigated spectroscopically and crystallographically to determine whether they were in the cis or trans configuration. Table 1 gives a summary of the results of this analysis and subsequent conformational assignments.

In a minimal basis set approach aromatic isocyanides contain a LUMO which is antibonding with respect to the N≡C bond, extending over the aromatic ring:
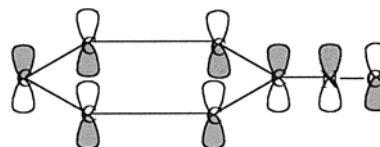
Aromatic isocyanides are, in general, better π-acids than aliphatic isocyanides, because of the enhanced ability of the ring to delocalize charge away from the transition-metal center. Aliphatic isocyanides are often bent significantly away from their expected linear geometries when coordinated to electron-rich metal centers, as charge localizes on the electronegative nitrogen atom, and there is sufficient electron pairing to result in rehybridization from sp toward sp^2. In most instances, aromatic isocyanides do not suffer this fate, since the ring is capable of delocalizing charge away from

Table 2. Coordinated Isocyanide Ligand Bond Lengths and Angles (Average Values)

isocyanide ligand	config	C_{phenyl}–N (Å)	N–$C_{isocyanide}$ (Å)	$C_{isocyanide}$–W (Å)	C–N–C (deg)
p-NCC$_6$H$_4$NC:	cis	1.346	1.274	1.892	136.8
p-CNC$_6$H$_4$NC:	cis	1.400	1.301	1.853	139.0
p-CNC$_6$H$_2$(CH$_3$)$_2$NC:	cis	1.405	1.219	1.963	143.9
p-F$_3$CC$_6$H$_4$NC:	cis	1.376	1.233	1.962	148.5
p-FC$_6$H$_4$NC:	trans	1.385	1.169	2.033	171.1
p-H$_3$CC$_6$H$_4$NC:	trans	1.392	1.246	1.992	167.1
p-H$_3$COC$_6$H$_4$NC:	trans	1.403	1.222	1.972	162.2
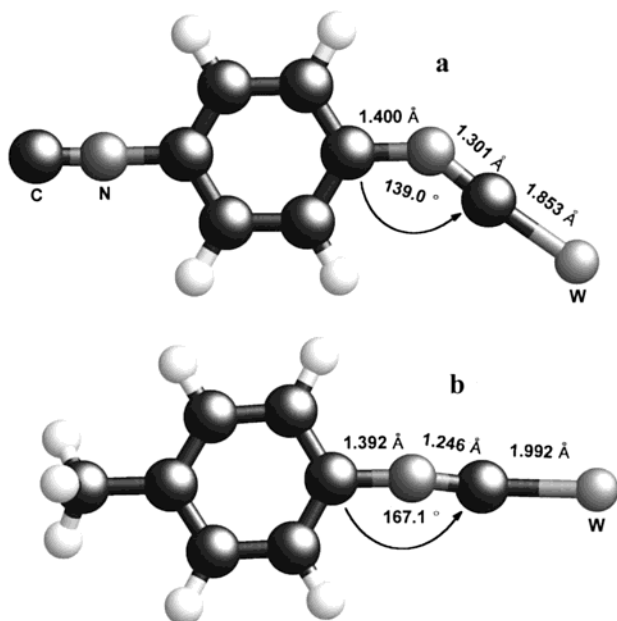
Figure 2. Geometry of the isocyanide ligands in (a) *cis*-(*p*-CNC$_6$H$_4$-NC)$_2$W(dppe)$_2$ and (b) *trans*-(*p*-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$.

the nitrogen atom. Figure 2a illustrates the geometry of the ligand found in *cis*-(*p*-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$.[3] It is clear that the ligand is incapable of delocalizing all of the charge "donated" from the electron-rich transition metal, and the ligand becomes substantially "distorted". This attests to the strong degree of electronic stabilization of the complex effected by the strong π-acidic *p*-CNC$_6$H$_4$NC: ligands. Figure 2b shows the geometry of the ligand found in *trans*-(*p*-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$,[16] illustrating that the weaker π-acid, *p*-H$_3$CC$_6$H$_4$NC:, does not undergo this distortion, since the charge withdrawal from the metal center is diminished. Crystal structures of a number of these complexes reveal that the ligands undergo these distortions in the cis conformation, but not in the trans conformation,[22] as summarized in Table 2.

The data given above provide a rigorous test for the application of the FMO formalism to organometallic complexes containing π-acidic ligands. If the electronic stabilization energy required to "force" the complexes into the sterically crowded cis conformation arises from the interaction of the donor HOMO (on the W(dppe)$_2$ fragment; constant for this series of complexes), and the ligand LUMO, then the relative energies of the LUMOs should reflect this. More importantly, these ligand LUMOs should serve as a predictive tool, allowing the investigator to determine the conformation of a complex by the ligand LUMO energy alone. The results of calculated ligand LUMO energies with various (GTO) basis sets are given in Table 3, based upon all-electron Hartree−Fock calculations, along with spectro-

Table 3. LUMO Energies for Isocyanide Ligands Calculated at the STO-3G, 6-31G, and 6-31G** levels[a]

ligand	STO-3G	6-31G	6-31G**	conformatn[b]
p-O$_2$NC$_6$H$_4$NC:	4.36	0.66	0.97	cis
p-NCC$_6$H$_4$NC:	4.35	1.08	1.16	cis
p-FO$_2$SC$_6$H$_4$NC:	4.57	0.44	1.29	
p-CNC$_6$H$_4$NC:	4.94	1.91	1.95	cis
p-HOOCC$_6$H$_4$NC:	5.29	1.95	2.05	
p-CNC$_6$H$_2$(CH$_3$)$_2$NC:	5.10	2.04	2.07	cis
p-F$_3$CC$_6$H$_4$NC:	5.34	1.77	2.16	cis
p-CNC$_6$(CH$_3$)$_4$NC:	5.31	2.34	2.36	trans
p-HSC$_6$H$_4$NC:	6.06	2.34	2.36	
p-IC$_6$H$_4$NC:	5.61			
p-BrC$_6$H$_4$NC:	5.62	2.39	2.43	
p-ClC$_6$H$_4$NC:	5.35	2.36	2.48	
p-HC$_6$H$_4$NC:	6.00	2.81	2.86	trans
p-FC$_6$H$_4$NC:	5.87	2.62	2.88	trans
p-H$_3$CC$_6$H$_4$NC:	6.06	2.93	2.96	trans
p-H$_3$COC$_6$H$_4$NC:	6.16	3.11	3.17	trans
CNC$_6$H$_{10}$NC:	9.90	4.92	5.05	

[a] Energies given are in electronvolts. [b] Experimentally determined.
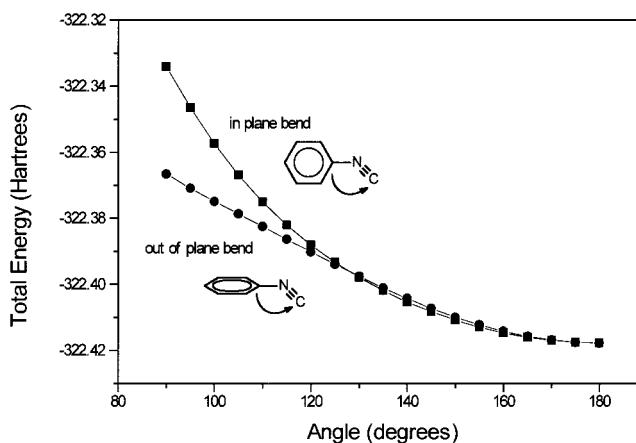
Figure 3. Calculated total energies of C$_6$H$_5$NC: as a function of ligand distortion at the 6-31G** level.

scopically or crystallographically determined geometries. While there are a few inversions in order for ligand LUMOs similar in energy, the same trend is observed, regardless of the level of the calculation. All those complexes with LUMO energies above 6.0 eV at the STO-3G level, 2.8 eV at the 6-31G level, and 2.8 eV at the 6-31G** level are apparently unable to provide enough electronic stabilization for the complex to overcome steric repulsions, and the ligands adopt a conformation in which they are trans to one another, despite being forced to compete for the same π-electron density. The smaller bends of the ligands also provide evidence of less back-bonding. Consistently, those with energies below 5.5 eV at the STO-3G level, 2.4 eV at the 6-31G level, and 2.4 eV at the 6-31G** level are sufficiently stabilized electronically to overcome steric repulsions, resulting in cis conformations.
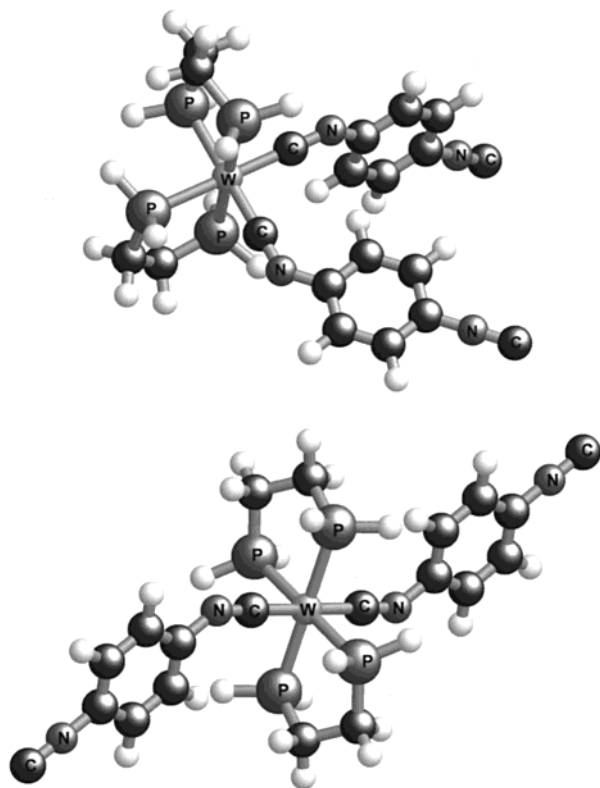
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Figure 4. Optimized geometries of *cis*- and *trans*-(*p*-CNC$_6$H$_4$-NC)$_2$W(H$_2$P(CH$_2$)$_2$PH$_2$))$_2$.

Even though the ligands become quite distorted in the cis complexes, the energy cost is apparently more than compensated for by the charge delocalization from the metal center. Figure 3 illustrates the effects of both in- and out-of-plane bends for the phenyl isocyanide ligand. In both cases bending to 120° raises the energy of the ligand by a little over 20 kcal mol^{-1}.

The steric constraints in these complexes result from the presence of the bulky dppe ligands. If the electronic versus steric hypothesis is valid, then the removal of the steric constraints in these complexes should result in conformations in which electronic stabilization dominates. To test this, density functional calculations with effective core potentials on tungsten were performed on a series of complexes in which the large phenyl groups on phosphorus were replaced with hydrogen atoms. The molecules were constrained to retain either cis or trans conformations; ligand bond lengths and angles were geometry optimized. Figure 4 illustrates the optimized structures for *cis*- and *trans*-(*p*-CNC$_6$H$_4$NC)$_2$W-(H$_2$P(CH$_2$)$_2$PH$_2$)$_2$; calculations with ligands containing various groups in the para position produced essentially the same conformations. Table 4 summarizes the results of these calculations. Removal of the phenyl groups from the phosphines renders the phosphine ligands less basic, thus decreasing the charge density at the metal. It is also of interest to note that there are significant in-plane bends in all of the ligands, implying that the experimentally observed near
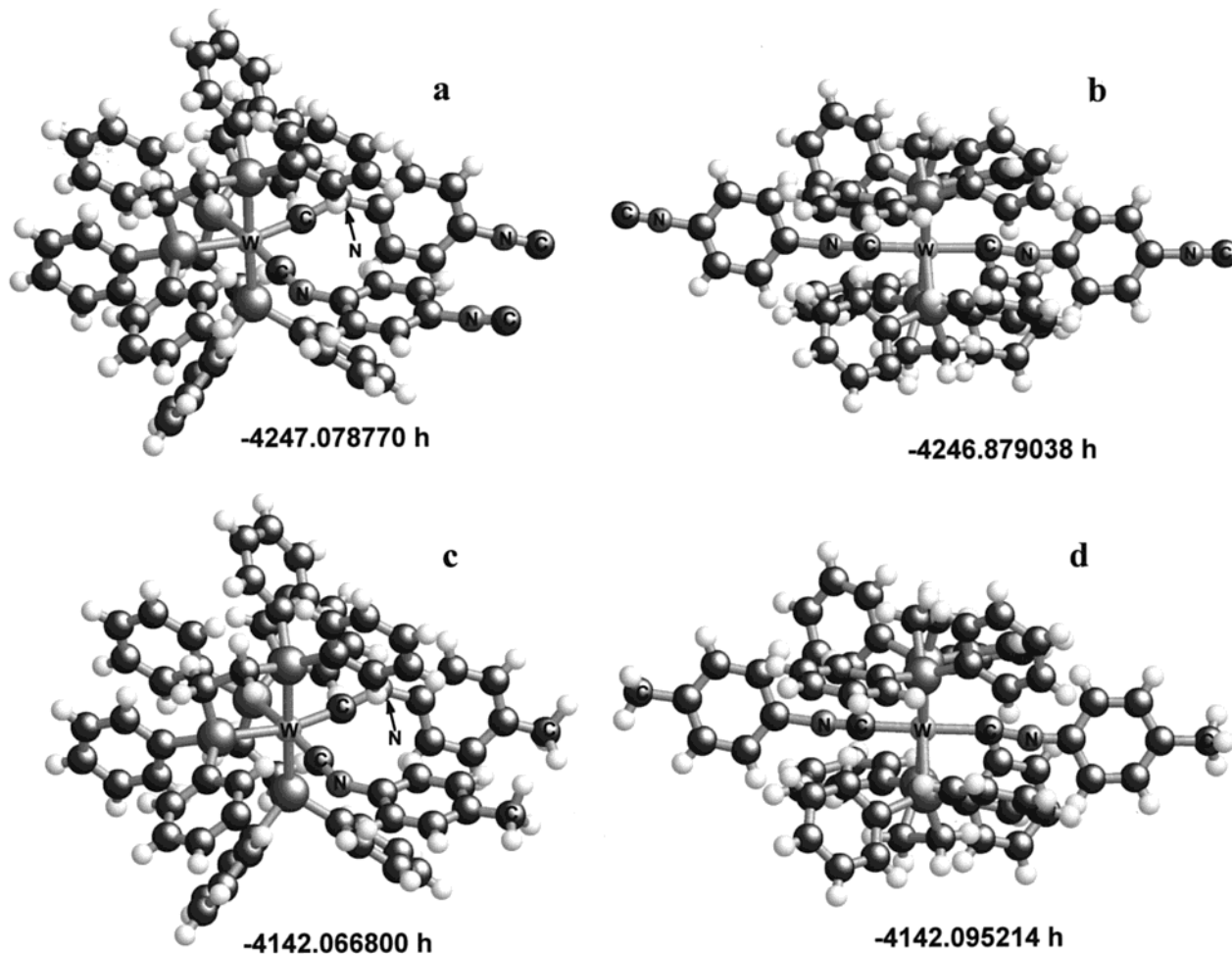

Figure 5. Structures and calculated title energies of (a) *cis*-(*p*-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$, (b) *trans*-(*p*-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$, (c) *cis*-(*p*-H$_3$-CC$_6$H$_4$NC)$_2$W(dppe)$_2$, and (d) *trans*-(*p*-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$.

Table 4. Ligand Parameters and Relative Energies (kcal mol^{-1}) For Geometry-Optimized *cis*- and *trans*-(p-RC$_6$H$_4$NC)$_2$W(H$_2$P(CH$_2$)$_2$PH$_2$)$_2$

ligand	config	W−C (Å)	C−N (Å)	N−C (Å)	C−N−C (deg)	rel energy
p-H$_3$CC$_6$H$_4$NC:	cis	1.954	1.235	1.378	136.38	0.00
p-H$_3$CC$_6$H$_4$NC:	trans	1.992	1.230	1.373	141.32	4.17
p-HC$_6$H$_4$NC:	cis	1.956	1.231	1.378	136.38	0.00
p-HC$_6$H$_4$NC:	trans	1.988	1.233	1.370	137.48	4.79
p-F$_3$CC$_6$H$_4$NC:	cis	1.944	1.239	1.373	135.42	0.00
p-F$_3$CC$_6$H$_4$NC:	trans	1.998	1.229	1.365	145.00	5.12
p-FC$_6$H$_4$NC:	cis	1.951	1.237	1.378	135.26	0.00
p-FC$_6$H$_4$NC:	trans	1.998	1.230	1.371	142.47	5.31
p-CNC$_6$H$_4$NC:	cis	1.943	1.240	1.373	134.82	0.00
p-CNC$_6$H$_4$NC:	trans	1.985	1.236	1.371	137.45	5.85

linearity in the trans molecules may arise largely from steric constraints, as does the configuration itself. Nevertheless, in the absence of steric constraints all of the complexes are more stable in the cis conformation, indicating that it is the electronically preferred configuration in all cases.

The next logical step in these studies was to add the phenyl groups back to the phosphine ligands and repeat the calculations, thus imposing the steric constraints which should force the molecules containing the weaker π-acids to adopt the trans conformation. Unfortunately, the size of the molecules presented a formidable barrier to geometry optimization. A less rigorous test, but computationally feasible, was to simply switch the para groups on *cis*-(p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ and *trans*-(p-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ (using crystallographic coordinates), perform single-point DFT calculations and compare the energies. Figure 5 illustrates the molecules with their calculated energies. In both cases the observed conformation is predicted by these calculations: The cis conformer of (p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ is more stable than the trans conformer by 124.8 kcal mol^{-1}, while the trans conformer of (p-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ is more stable than the cis conformer by 17.8 kcal mol^{-1}. It should be noted here that the use of pseudopotentials for tungsten accounts for relativistic effects only implicitly, so that the absolute magnitudes of these energies may be somewhat suspect. Nevertheless, the relative magnitude of these numbers is reasonable, since the trans conformer would not be expected to be significantly more stable than the cis conformer, driven only by relative steric repulsions. While geometry optimization might result in relaxations which would lower the magnitude of the stabilization energy of the trans isomer, its value is reasonable in light of the significant geometric changes that occur when the cis conformation is adopted. The W−C bond lengths in the cis complexes are significantly shorter than those in the trans complexes,[3] and the resulting increase in bond order could certainly result in a ca. 100 kcal mol^{-1} difference.

CONCLUSIONS

By comparing the LUMO energies of a series of π-acids, calculated even at the minimal basis set level, it is possible to predict the relative stabilization energies induced by coordination of these ligands onto zerovalent tungsten. Density functional calculations on a series of these complexes in which steric constraints were removed indicated that all π-acids tend to coordinate cis to one another to maximize the electronic stabilization energy. Weaker π-acids, in the

presence of bulky ligands, adopt the trans geometry, supporting the premise that steric repulsion will dominate the geometry of the complex when there is insufficient electronic stabilization. The π-acidities of these ligands are dictated by the nature of the para substituent, with density functional calculations providing relative energies consistent with the observed geometries of these complexes, with the caveat that the complexes created by switching these substitients were not geometry optimized. This does suggest that a combination of molecular mechanics calculations for geometry optimization, coupled with single-point DFT calculations, would be useful in determining the geometric and electronic structures of large transition-metal complexes, such as those studied in this investigation. In addition, recent advances in density functional theory[23−25] have shown that one can provide a more rigorous description of the LUMO at the DFT level than at the HF level. We will reexamine the HOMOs and LUMOs of the various ligands, as well as the energy differences (gap) between the HOMO and LUMO of each ligand at the DFT level and report on these in a subsequent paper.

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