Conformational Isomerism in (p-$RC_6H_4NC)_2W(dppe)_2$: Substantial Structural Changes Resulting from Subtle Differences in the π-Acidity of p-RC_6H_4NC

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Received June 2, 2000

Abstract: Bis(arylisocyanide) complexes of tungsten containing bulky bidentate aryl phosphine ligands adopt either cis or trans conformations, depending on the nature of the *para*-substituent group on the aryl isocyanide ligand. Ab initio calculations on a series of ligands, p-RC_6H_4NC, indicate that the energy of the LUMO is determined by the electron-withdrawing/donating capabilities of the substituent group, which determine the relative π-acidity of the ligand. 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. Weaker π acids, containing donor substituents, do not provide enough electronic stabilization to overcome steric repulsion, resulting in the adoption of trans geometry. $(CNC_6H_4NC)W(dppe)_2$ exists as the cis conformer, as does $(CNC_6H_2(CH_3)_2NC)W(dppe)_2$, while $(CNC_6(CH_3)_4$-$NC)W(dppe)_2$, with increased steric bulk coupled with decreased π-acidity, exists as the trans conformer. Theoretical and experimental studies indicate that the energy match between isocyanide ligands and the metal center can be modified significantly by the selection of various substituents and that relatively subtle variations in the electronic structure of the ligands can have dramatic effects on the structures of the resulting complexes.

Introduction

Aromatic diisocyanide ligands are capable of bridging transition metal centers and mediating communication between those centers through a conjugated dπ−pπ−dπ network.[1] Recently, we have shown that these ligands are also effective molecular-level conductors.[2] Current research in our laboratories is centered around the exploitation of these properties to create tunable, electrode-bound electrocatalysts, in which activity and selectivity can be modified by varying electrode voltage through the diisocyanide ligand which couples the complex to the electrode surface. We are also working toward the synthesis of one-dimensional, insulated, organometallic molecular-level wires, in this case making use of the diisocyanide as a conductive bridge between transition metal centers.[3] Ideally, for both of these applications, the molecular species should contain electron rich metal centers (i.e., be as “metal-like” as possible), and should be resistant to external oxidation, yet able to undergo selective hole formation through the conjugated system. In addition, for optimal charge polarization/transfer, the bridging ligands should be alterable, to modulate metal−ligand coupling,[4] and they should be trans to one another. We previously reported the creation of monometallic precursors, (p-$CNC_6H_4NC)_2W$-$(dppe)_2$ and the analogous (p-$NCC_6H_4NC)_2W(dppe)_2$, designed to create these new oligomeric/polymeric species.[5] While these monomers are indeed electron rich and kinetically robust toward external oxidation, crystal structures of both molecules reveal that they preferentially adopt a conformation in which the isocyanide ligands are cis to one another. The coordinated isocyanides in both of these molecules exhibit remarkably short metal−carbon bonds and a substantial distortion of the ligand geometry, indicating a strong electronic stabilization driven by the ability of the isocyanide to polarize charge away from an electron-saturated tungsten center. It follows that these molecules would be ideal building blocks for molecular-level wires and tunable catalysts, were it not for their proclivity to adopt cis geometries. The bulky bidentate phosphine ligands in these complexes create severe steric constraints when the ligands are cis to one another, and in the absence of substantial electronic effects, these complexes would all be expected to coordinate the isocyanide ligands trans to one another. Electronic stabilization of low-valent transition metal complexes usually depends on the ability of ligands in the coordination sphere to polarize negative charge away from an electron-rich metal center, i.e., to behave as π acids. On the basis of this premise, ligands which behave as weak π acceptors would be expected to adopt the sterically favored *trans* conformation, while strong π acids could engender enough electronic stabilization to overcome steric repulsions and coordinate cis to one another. In this paper we describe the results of an investigation of this hypothesis and demonstrate that the application of the resulting model allows for the design and synthesis of thermodynamically stable trans aromatic diisocyanide complexes. We also report the results of a study designed to determine the key elements of the mechanism of formation of these complexes, which ultimately has led to the creation of kinetically robust trans aromatic diiso-

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[1] Grubisha, D. S.; Rommel, J. S.; Lane, T. M.; Tysoe, W. T.; Bennett, D. W. *Inorg. Chem.* **1992**, *31*, 5022.

[2] Chen, J.; Calvet, L. C.; Reed, M. A.; Carr, D. W.; Grubisha, D. S.; Bennett, D. W. *Chem. Phys. Lett.* **1999**, *313*, 741.

[3] Wagner, N. L.; Laib, F. E.; Bennett, D. W. *Inorg. Chem. Commun.* **2000**, *3*, 87.

[4] Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60.

10.1021/ja0018466 CCC: $19.00

cyanide complexes which would otherwise adopt the thermodynamically favored cis conformation.

Materials and Methods

General Reagents and Procedures. 1,2-Bis(diphenylphosphino)ethane was purchased from Strem Chemicals; 1,4-phenylenediamine was purchased from Fluka Chemical; tungsten (VI) chloride, PPh$_3$, and benzyltriethylammonium chloride were purchased from Aldrich Chemical Co.; *p*-nitroaniline, *p*-toluidine, *p*-anisidine, 4-fluoroaniline, and 4-aminobenzotrifluoride were purchased from Fisher Scientific; solvents were purchased from VWR Scientific. The following reagents were prepared according to literature procedures: *trans*-(N$_2$)$_2$W(dppe)$_2$,[6] NO$_2$C$_6$H$_4$NC,[7] CNC$_6$H$_4$NC,[7] CNC$_6$H$_2$(CH$_3$)$_2$NC,[7] CNC$_6$(CH$_3$)$_4$NC,[7] CH$_3$C$_6$H$_4$NC,[8] CH$_3$OC$_6$H$_4$NC,[8] FC$_6$H$_4$NC,[8] and CF$_3$C$_6$H$_4$NC.[8] The syntheses of (CH$_3$C$_6$H$_4$NC)$_2$W(dppe)$_2$ and (CH$_3$OC$_6$H$_4$NC)$_2$W(dppe)$_2$ have been previously reported,[9] although the synthesis reported here is slightly different. All reactions were performed under an atmosphere of dry oxygen-free nitrogen using standard Schlenck techniques. Solvents were deoxygenated and dried by distillation from sodium benzophenone or P$_2$O$_5$. Infrared spectra were recorded from KBr pellets on a Nicolet MX-1 FTIR spectrometer. ^{31}P NMR spectra were recorded on a Bruker WM 300-MHZ NMR spectrometer with 85% H$_3$PO$_4$(aq) as the external reference. Electronic absorption spectra were obtained on a Hewlett-Packard 8451A spectrometer. LSIMS spectra were collected on a VG Autospec mass spectrometer. X-ray data were collected on Picker and Siemens SMART CCD diffractometers. Calculations were performed using the Gaussian 98 program.[10] All ligands were geometry optimized. Single point density functional calculations were performed on the transition metal complexes using BECKE3LYP, based on a hybrid three parameter functional,[11] together with the LANL2DZP ECP and basis set.[12]

***cis*-(CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ (1).** There were slight modifications of this synthesis from that previously reported.[5] *trans*-(N$_2$)$_2$W(dppe)$_2$ (0.30 g, 0.29 mmol) and CNC$_6$H$_4$NC (0.37 g, 2.9 mmol) were vigorously refluxed in 80 mL of THF for 24 h. The solvent volume was reduced to ca. 30 mL. Hexane (50 mL) was added to give dark red crystals of *cis*-(CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ (32% yield). ^{31}P NMR δ (ppm): 32.1 ($J_{PP} = 6.0$ Hz, $J_{WP} = 194$ Hz), 47.5 ($J_{PP} = 5.9$ Hz, $J_{WP} = 280$ Hz). IR (cm^{-1}): ν_{CN} 2120 m (terminal CN), 1763 m, 1662 m. LSIMS: [M]$^+$ $m/z = 1236$.

***cis*-(F$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ (2).** Orange crystals of the complex were prepared in a manner identical to that for **1**, substituting CF$_3$C$_6$H$_4$NC for CNC$_6$H$_4$NC (41% yield). ^{31}P NMR δ (ppm): 32.2 ($J_{WP} = 188$ Hz), 47.7 ($J_{WP} = 273$ Hz). IR (cm^{-1}): ν_{CN} 1834 m, 1693 m. LSIMS: [M]$^+$ $m/z = 1322$.

***cis*-(O$_2$NC$_6$H$_4$NC)$_2$W(dppe)$_2$ (3).** The complex was prepared in a manner identical to that for **1**, substituting O$_2$NC$_6$H$_4$NC for CNC$_6$H$_4$NC. The dark brown compound was further purified by recrystallization from 1:2 THF/hexane. There were inseparable byproducts in this reaction which prohibited complete isolation of the complex. Analysis of the mass spectrum of the reaction mixture indicated that partial oxidation of the tungsten complex occurred. Essenmacher and Treichel reported similar oxidations of Cr(0) complexes when they were allowed to react with aryl isocyanides which contained strongly electron-withdrawing substituents.[13] ^{31}P NMR δ (ppm): 30.8, 47.4. IR (cm^{-1}): ν_{CN} 1743 m, 1662 m. LSIMS [M]$^+$ $m/z = 1276$.

Table 1. Crystallographic Details for (*p*-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ and (*p*-H$_3$COC$_6$H$_4$NC)$_2$W(dppe)$_2$

	(*p*-H$_3$CC$_6$H$_4$NC)$_2$W-(dppe)$_2$	(*p*-H$_3$COC$_6$H$_4$NC)$_2$W-(dppe)$_2$
formula	C$_{68}$H$_{62}$N$_2$P$_4$W	C$_{68}$H$_{62}$N$_2$O$_2$P$_4$W
molar mass	1214.96	1246.96
a, Å	19.947(2)	10.499(2)
b, Å	16.455(2)	11.275(2)
c, Å	21.419(2)	13.552(2)
α, deg	90.000	65.53(1)
β, deg	101.125(8)	86.49(2)
γ, deg	90.00	77.33(2)
V, Å^3	6896.6	1582.636
space group	A_n	$P1$
Z	4	1
ρ_{calcd}, g cm^{-3}	1.170	1.454
μ, mm^{-1}	4.25	5.24
λ, Å	1.541 78	1.541 78
T, K	298	298
reflns collected	3538	2436
unique reflns	3538	2436
no. of params	706	351
$2\theta_{max}$, deg	104.99	100.15
$R1^a$ ($I > 2\sigma(I)$)	0.0536	0.124
$wR2^b$	0.1300	0.296

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)/\Sigma[w(F_o{}^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (a_1P)^2 + a_2P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

***trans*-(FC$_6$H$_4$NC)$_2$W(dppe)$_2$ (4).** Orange crystals of the complex were prepared in an identical manner to **1**, substituting FC$_6$H$_4$NC for CNC$_6$H$_4$NC (38% yield). ^{31}P NMR δ (ppm): 51.0. IR (cm^{-1}) ν_{CN} 1970 w, 1865 s. LSIMS [M]$^+$ $m/z = 1222$.

***trans*-(CH$_3$C$_6$H$_4$NC)$_2$W(dppe)$_2$ (5).** Red crystals of the complex were prepared in a manner identical with that for **1**, substituting CH$_3$C$_6$H$_4$NC for CNC$_6$H$_4$NC (37% yield). ^{31}P NMR δ (ppm): 47.9 ($J_{WP} = 290$ Hz). IR (cm^{-1}): ν_{CN} 1952 w, 1873 s. LSIMS [M]$^+$ $m/z = 1214$.

***trans*-(CH$_3$OC$_6$H$_4$NC)$_2$W(dppe)$_2$ (6).** Red crystals of the complex were prepared in a manner identical with that for **1**, substituting CH$_3$OC$_6$H$_4$NC for CNC$_6$H$_4$NC (32% yield). ^{31}P NMR δ (ppm): 47.2; IR (cm^{-1}) ν_{CN} 1951 w, 1822 s. LSIMS [M]$^+$ $m/z = 1246$.

***cis*-(*p*-CNC$_6$H$_2$(CH$_3$)$_2$NC)$_2$W(dppe)$_2$ (7).** Purple crystals of the complex were prepared in an identical manner to **1**, substituting CNC$_6$H$_2$(CH$_3$)$_2$NC for CNC$_6$H$_4$NC (36% yield). ^{31}P NMR δ (ppm): 32.0 ($J_{PP} = 7.4$ Hz, $J_{WP} = 188$ Hz), 46.2 ($J_{PP} = 7.6$ Hz, $J_{WP} = 278$ Hz). IR (cm^{-1}): ν_{CN} 1772 m, 1669 m. LSIMS [M]$^+$ $m/z = 1292$.

***trans*-(*p*-CNC$_6$(CH$_3$)$_4$NC)$_2$W(dppe)$_2$ (8).** The complex was prepared in a manner identical with that for **1**, substituting CNC$_6$(CH$_3$)$_4$NC for CNC$_6$H$_4$NC. The purple compound was further purified by recrystallization from 1:2 THF/hexane. ^{31}P NMR δ (ppm): 45.5 ($J_{WP} = 321$ Hz). IR (cm^{-1}): ν_{CN} 1819 s, 1943 w. LSIMS [M]$^+$ $m/z = 1349$.

X-ray Structural Determination of (H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ and (H$_3$COC$_6$H$_4$NC)$_2$W(dppe)$_2$. Crystallographic and other experimental data are summarized in Table 1. Single crystals were mounted in capillary tubes which were then sealed with epoxy to prevent decomposition of the crystal. X-ray data were collected on a Picker diffractometer using PCXTL.[14] Orientation and crystal decay were monitored by measuring the intensities of three reference reflections at 120-min intervals. Minimal intensity losses were observed. Data reduction, handling, and analysis were performed using NRCVAX.[15]

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(5) Hu, C.; Hodgeman, W. C.; Bennett, D. W. *Inorg. Chem.* **1996**, *35*, 1621.

(6) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, 119.

(7) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offerman, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472.

(8) Weber, W. P.; Gokel, G. W. *Tetrahedron Lett.* **1972**, *17*, 1637.

(9) Chatt, J.; Elson, C. M.; Pombeiro, A. J. L.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1978**, 165.

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

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(12) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(13) Essenmacher, G. J.; Treichel, P. M. *Inorg. Chem.* **1977**, *16*, 800.

(14) Weinrach, J. B.; Bennett, D. W. *J. Appl. Crystallogr.* **1991**, *24*, 91.

(15) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Table 2. Crystallographic Details for (p-$CNC_6H_2(CH_3)_2NC)_2W(dppe)_2$, ($p$-$F_3CC_6H_4NC)_2W(dppe)_2$ and (p-$FC_6H_4NC)_2W(dppe)_2$

	(p-$CNC_6H_2(CH_3)_2NC)_2W(dppe)_2$	(p-$F_3CC_6H_4NC)_2W(dppe)_2$	(p-$FC_6H_4NC)_2W(dppe)_2$
formula	$C_{72}H_{68}N_4P_4W$	$C_{68}H_{56}F_6N_2P_4W$	$C_{66}H_{56}N_2F_2P_4W$
molar mass	1293.04	1322.91	1222.89
a, Å	18.2616(3)	10.1749(2)	12.2171(5)
b, Å	19.8095(6)	24.5966(5)	12.3213(5)
c, Å	20.5076(6)	24.7983(5)	19.6284(7)
α, deg	90.000	90.000	90.000
β, deg	112.490(2)	90.000	90.403(1)
γ, deg	90.000	90.000	90.000
V, Å^3	6854.5	6206.2	2954.6
space group	$C_{2/c}$	P_{212121}	$P_{2/c}$
Z	4	4	2
ρ_{calcd}, g cm^{-3}	1.257	1.416	1.375
μ, mm^{-1}	1.82	2.02	2.11
λ, Å	0.710 73	0.710 73	0.710 73
T, K	198	198	198
reflns collected	19 046	39 319	18 832
unique reflns	6517	14311	6763
no. of params	367	731	339
$2\theta_{max}$, deg	51.37	55.81	55.84
R1^a ($I > 2\sigma(I)$)	0.1012	0.0571	0.0731
$wR2^b$	0.2943	0.1595	0.2066

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma(w(F_o^2 - F_c^2)/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (a_1P)^2 + a_2P]$ where $P = (F_o^2 + 2F_c^2)/3$.

The locations of the tungsten and phosphorus atoms were determined by direct methods using SHELXS-86.[16] The remaining non-hydrogen atoms were located by using a combination of tangent expansion and difference Fourier techniques. The structures were refined using SHELXL-97.[17] All heavy atoms were refined anisotropically. Hydrogen atoms were allowed to ride with the heavy atom to which they were bonded. Structural drawings were made using ORTEP.[18]

X-ray Structural Determination of ($CNC_6H_2(CH_3)_2NC)_2W$-($dppe)_2$, ($F_3CC_6H_4NC)_2W(dppe)_2$, and ($FC_6H_4NC)_2W(dppe)_2$. Crystallographic and other experimental data are summarized in Table 2. Single crystals were mounted on the tip of a capillary under nitrogen with epoxy, and placed immediately onto a Siemens SMART CCD detector diffractometer, equipped with a cryogenic nitrogen cold stream. Structural solution, refinement, and graphical methods were identical to those described above.

Results and Discussion

1. Thermodynamic Considerations. I. Computational Studies. The frontier molecular orbital formalism suggests that the π acidity of the isocyanide ligands should increase as their unoccupied π^* virtual orbitals decrease in energy, providing a better energy match for filled metal d orbitals. In 1991 Johnston and Cooper[19] reported the results of minimal basis set (STO-3G) calculations on a series of isocyanide ligands, predicting that the relative π acidities of these ligands would parallel the energies of their π^* LUMOS. The ligands in this study were investigated similarly, using extended basis sets with Gaussian 98;[10] the results are given in Table 3.

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**
p-O_2N-C_6H_4NC:	4.36	0.66	0.97
p-NC-C_6H_4NC:	4.35	1.08	1.16
p-FO_2S-C_6H_4NC:	4.57	0.44	1.29
p-CN-C_6H_4NC:	4.94	1.91	1.95
p-HOOC-C_6H_4NC:	5.29	1.95	2.05
p-CN-$C_6H_2(CH_3)_2NC$:	5.10	2.04	2.07
p-F_3C-C_6H_4NC:	5.34	1.77	2.16
p-CN-$C_6(CH_3)_4NC$:	5.31	2.34	2.36
p-HS-C_6H_4NC:	6.06	2.34	2.36
p-I-C_6H_4NC:	5.61		
p-Br-C_6H_4NC:	5.62	2.39	2.43
p-Cl-C_6H_4NC:	5.35	2.36	2.48
p-H-C_6H_4NC:	6.00	2.81	2.86
p-F-C_6H_4NC:	5.87	2.62	2.88
p-H_3C-C_6H_4NC:	6.06	2.93	2.96
p-H_3CO-C_6H_4NC:	6.16	3.11	3.17
$CNC_6H_{10}NC$:	9.90	4.92	5.05

^{a} Energies given are in electronvolts.

In previous crystallographic studies the isocyanide ligands bonded in complexes (p-$CNC_6H_4NC)_2W(dppe)_2$ and (p-NCC_6H_4-$NC)_2W(dppe)_2$ were observed to undergo significant structural changes.[5] The C−N bond length of the isocyanide group bound to the tungsten center in these complexes increased from 1.1 Å in the free ligand to 1. 3 Å upon coordination, approaching the length of a carbon−nitrogen single bond. The C−N−C bond angle bent from characteristic linearity to an extraordinary 137−139 degrees, and the metal−carbon bond length in these complexes averaged 1.85 Å, significantly shorter than the ca. 2.1 Å typical of tungsten isocyanide bonds. Both complexes adopted a cis conformation, apparently foregoing the more sterically favorable trans geometry to gain electronic stabilization, despite experiencing tremendous ligand distortions. This preference for cis geometry often results when two strong π acids compete for π electron density, in which case they both opt for coordination opposite stronger donor ligands.[20] Surprisingly, a third complex in which the terminal isocyanide/nitrile groups were replaced by methyl groups provided spectroscopic evidence characteristic of a trans complex (see below). The methyl group is less electron withdrawing than the CN groups, hinting that there might be a subtle balance between steric and electronic stabilization in these complexes. It follows that the tendency of (p-$RC_6H_4NC)_2W(dppe)_2$ to adopt a cis configuration should increase as the energy of the π^* LUMO decreases, approaching the lower energy of the occupied metal-like frontier orbitals on the metal and resulting in increased charge polarization away from the metal center into the isocyanide π system.

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(16) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(17) Sheldrick, G. M. SHEXL97, A Program for Crystal Structure Refinement; University of Gottingen, Germany, 1997.

(18) Johnson, C. K. ORTEP II Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(19) Johnston, R. F.; Cooper, J. C. *J. Mol. Struct. (THEOCHEM)* **1991**, *236*, 297.

(20) Guy, M. P.; Guy, J. T., Jr.; Bennett, D. W. *Organometallics* **1986**, *5*, 1696.

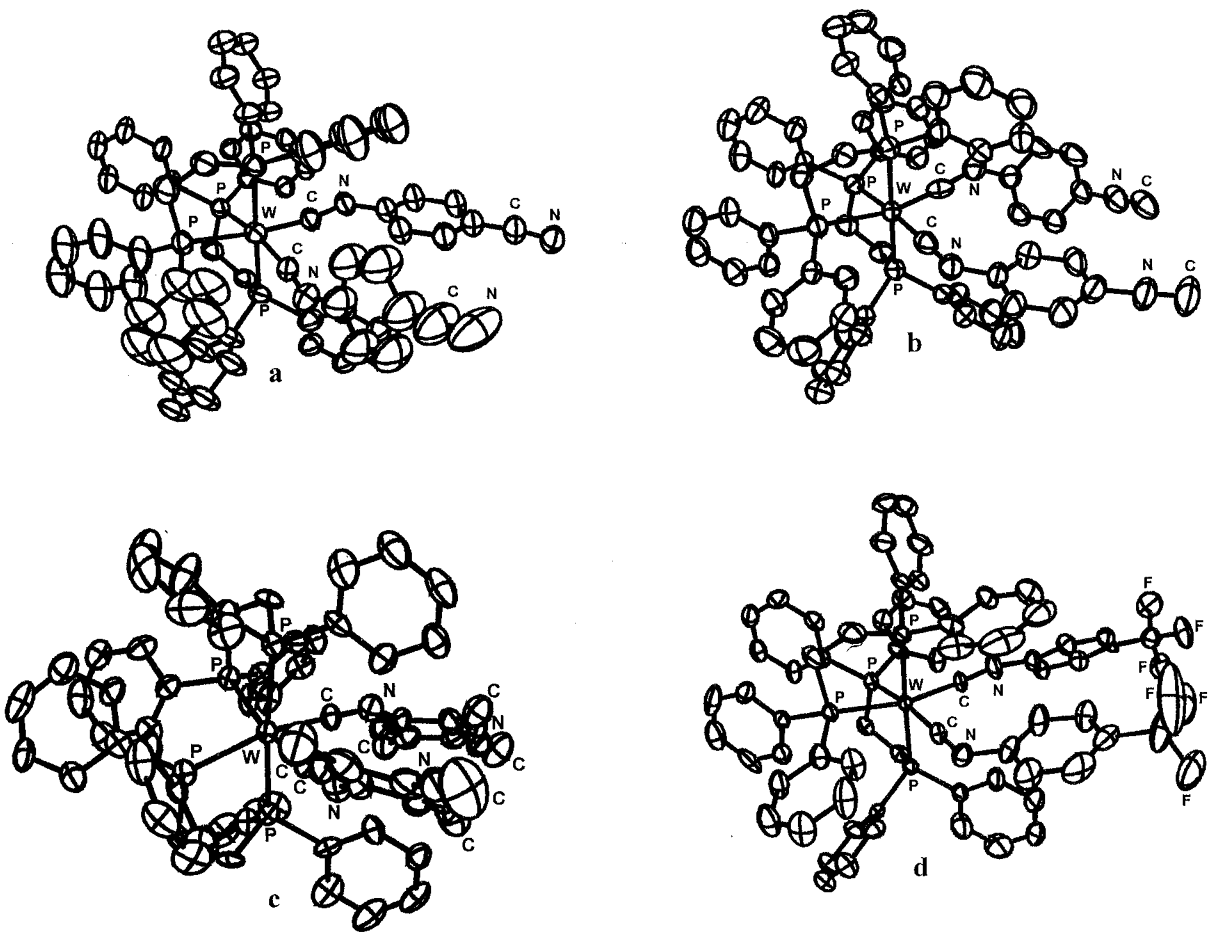

Figure 1. X-ray crystal structures (ORTEP diagrams) of (a) (p-NCC$_6$H$_4$NC)$_2$W(dppe)$_2$, (b) (p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$, (c) (p-NCC$_6$H$_2$(CH$_3$)$_2$-NC)$_2$W(dppe)$_2$, and (d) (p-F$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ complexes adopting the cis conformation.

II. Structural Investigations. To investigate the hypothesis stated above, a series of diisocyanide complexes of the form (p-RC$_6$H$_4$NC)$_2$W(dppe)$_2$ was created, in which R varies in its electron donating/withdrawing capabilities. Crystal structures of several of these complexes were obtained; molecules with the isocyanide ligands cis to one another are illustrated in Figure 1; molecules with the isocyanide ligands trans to one another are illustrated in Figure 2. The "preferred" conformation of each of these complexes is entirely consistent with the relative energies of the LUMOs of the isocyainde ligands in the complexes; those with higher LUMO energies adopt *trans* configurations, those with lower LUMO energies are in the cis conformation, as predicted.

Figure 3 compares the W−C−N−C$_6$H$_n$(CH$_3$)$_{4-n}$−R moieties, illustrating the M−C distances and ligand distortions in each complex. The cis complexes all contain strong electron-withdrawing groups and display major ligand distortions. This is atypical of coordinated aromatic isocyanides, which are generally capable of delocalizing excess charge density from M−L back-donation into the aromatic ring system. Coordinated aliphatic isocyanides are often distorted in a manner similar to that observed here, the distortions arising from charge localization on the electronegative nitrogen atom closest to the M−C bond and subsequent pairing effects which tend to "rehybridize" the nitrogen atom from sp toward sp^2 hybridization. Consequently, it appears that there is so much excess charge density at the metal center in the complexes studied in this investigation that the aromatic ring is incapable of accommodating all of the excess charge when significant back-bonding occurs, leaving behind enough electron density on the nitrogen atoms to result in similar bends. To determine if the balance between electronic and steric factors could be altered by increasing the size of the ligands in the *cis* complexes, the isocyanide ligands in (p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ were replaced with dimethylated ligands, forming (p-CNC$_6$H$_2$(CH$_3$)$_2$NC)$_2$W(dppe)$_2$ (Figures 1b and 3c). Since the methyl groups on the ligands would increase their steric repulsions and behave as electron donors, thus increasing the energy of the LUMO (Table 3), we anticipated that the ligands would coordinate trans to one another. Surprisingly, the ligands remained in the cis positions, even though they experienced significant "out-of-plane" distortions: The angle between C$_{\text{phenyl}}$ and (N−C)$_{\text{projected}}$ (the projection of the C−N−C$_{\text{phenyl}}$ positions onto a plane orthogonal to the ring) is 24.56°. As we have shown in previous work,[21] as long as the bend remains "in-plane," the distortion requires very little change in M−L π overlap, costing the molecule little in energy to distort compared to its energetic gains as electron−electron repulsion is lowered at the metal center due to strong M−L back-bonding. However, out-of-plane bends do result in significant strain energies. Thus, even when the distortion energy costs are quite severe, the ability of the isocyanide group to polarize charge away from the metal center is apparently stabilizing enough to compensate for this energy. The electron-withdrawing CF$_3$ groups in (p-F$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$ also result in steric crowding, but again, the ligands remain cis to one another. In this case, evidently to accommodate one another,

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[21] Guy, M. P.; Guy, J. T., Jr.; Bennett, D. W. *J. Mol. Struct. (THEOCHEM)* **1985**, *122*, 95.

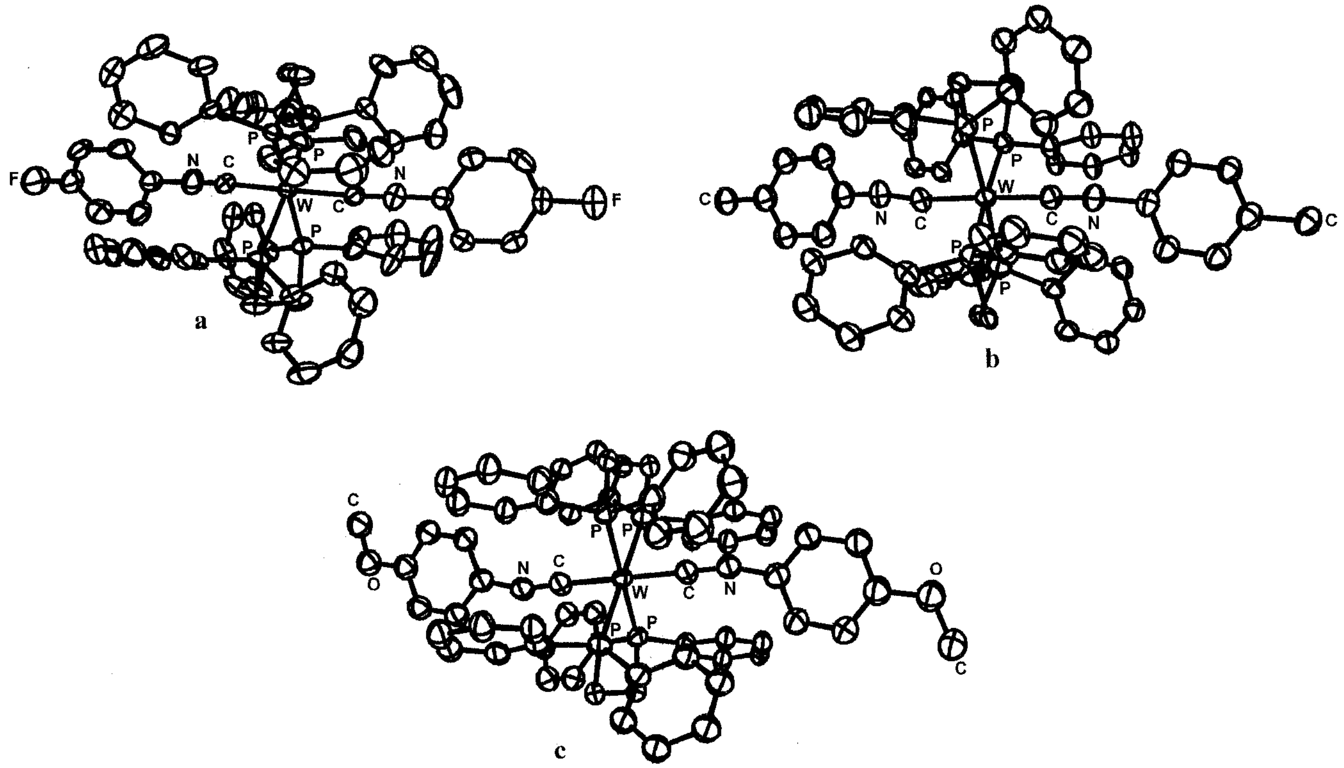

Figure 2. X-ray crystal structures (ORTEP diagrams) of (a) (p-$FC_6H_4NC)_2W(dppe)_2$, (b) (p-$H_3CC_6H_4NC)_2W(dppe)_2$, and (c) (p-$H_3COCC_6H_4$-$NC)_2W(dppe)_2$ complexes adopting the trans conformation.

one ligand remains almost linear, while the other bends to 132° the largest bend of any of the complexes studied (Figures ld and 3d,e). The *average* $C-N-C_{phenyl}$ angles vary in the order p-NCC_6H_4NC (137°) < p-CNC_6H_4NC (139°) < p-$CNC_6H_2(CH_3)_2NC$ (144°) < p-$CF_3C_6H_4NC$ (149°) in the cis complexes. The isocyanide ligands in the trans complexes, (p-$FC_6H_4NC)_2W(dppe)_2$, (p-$H_3CC_6H_4NC)_2W(dppe)_2$, and (p-$CH_3OC_6H_4NC)_2W(dppe)_2$, remain nearly linear, exhibiting only slight ligand distortions which are probably due to a combination of packing forces and excess electron density on the isocyanide nitrogen atom. The results of these structural studies are all consistent with the "π-acidity" hypothesis. Of the complexes which yielded crystal structures, those with isocyanide ligands which have LUMO energies less than ca. 2.3 eV (at the 6-31G** level) adopt the cis conformation, while those with LUMO energies above 2.8 eV adopt the trans conformation. The relative energy of the LUMO in each of these complexes appears to be an accurate indicator of the tendency of a given pair of ligands to adopt either the sterically favored *trans* conformation or the electronically stabilized cis conformation.

III. NMR Spectroscopic Studies. The conformations of these complexes in solution are readily determined from their phosphorus NMR spectra. As in the solid-state studies discussed in the previous section, the ^{31}P NMR spectra illustrate that the conformations of these complexes are reliably predicted by the relative energies of the isocyanide ligand LUMOs.

The major features of the ^{31}P NMR spectra of the complexes studied in this investigation are summarized in Table 4. The spectra of (p-$RC_6H_4NC)_2W(dppe)_2$ exhibit two distinct patterns, depending on the nature of the *para*-substituent. For R = p-$O_2NC_6H_4NC$, p-CNC_6H_4NC, p-$CNC_6H_2(CH_3)_2NC$, or p-$F_3CC_6H_4NC$, two sharp resonances of equal intensity are observed, one at 30−33 ppm, the other at 46−48 ppm (downfield from external H_3PO_4). Tungsten−phosphorus coupling constants are in the 270−280 Hz range for the downfield resonance and in the 180−200 Hz range for the upfield signal. The presence of the two resonances is consistent with cis geometry for the complexes, where the upfield resonance is assigned to the phosphorus atoms trans to the isocyanides and the downfield resonance is assigned to the mutual trans phosphorus atoms. For R = p-$CNC_6(CH_3)_4NC$, p-$H_3COC_6H_4$-NC, p-$H_3CC_6H_4NC$, or p-FC_6H_4NC, a single ^{31}P signal at 45−51 ppm is observed, indicating four chemical-shift equivalent phosphorus nuclei, consistent with a trans conformation. Unlike the sharp resonances for the *cis* complexes, the single peak for the trans complexes is substantially broader at ambient temperature, sharpening when the temperature is lowered. This implies a dynamic exchange process, which will be discussed in part 2. J_{WP} for these complexes ranges from 270 to 321 Hz, characteristic of phosphorus atoms trans to one another, as discussed above. Consistent with the crystallographic studies, the ^{31}P NMR data indicate cis conformations for those complexes with 631G** LUMO energies below 2.3 eV and trans geometries for those with LUMO energies above 2.8 eV.

Table 4. ^{31}P NMR Chemical Shifts for *cis*- and *trans*-(p-R-$C_6H_4NC)_2W(dppe)_2$

isocyanide ligand	configuration	^{31}P chemical shift,[a] ppm	J_{WP}, Hz
p-O_2N-C_6H_4NC:	cis	30.8, 47.5	U[b]
p-CN-C_6H_4NC:	cis	32.1, 47.5	196, 280
p-CN-$C_6H_2(CH_3)_2NC$:	cis	32.0, 46.2	188, 278
p-F_3C-C_6H_4NC:	cis	32.2, 47.7	188, 273
p-CN-$C_6(CH_3)_4NC$:	trans	45.5	321
p-F-C_6H_4NC:	trans	51.0	U[b]
p-H_3C-C_6H_4NC:	trans	47.9	290
p-H_3CO-C_6H_4NC:	trans	47.2	U[b]

[a] Relative to 85% H_3PO_4 (0.0 ppm); ^{31}P NMR spectra acquired in THF. [b] Not observed.

IV. Infrared Spectroscopic Studies. The infrared spectra of the complexes studied in this investigation exhibit charac-

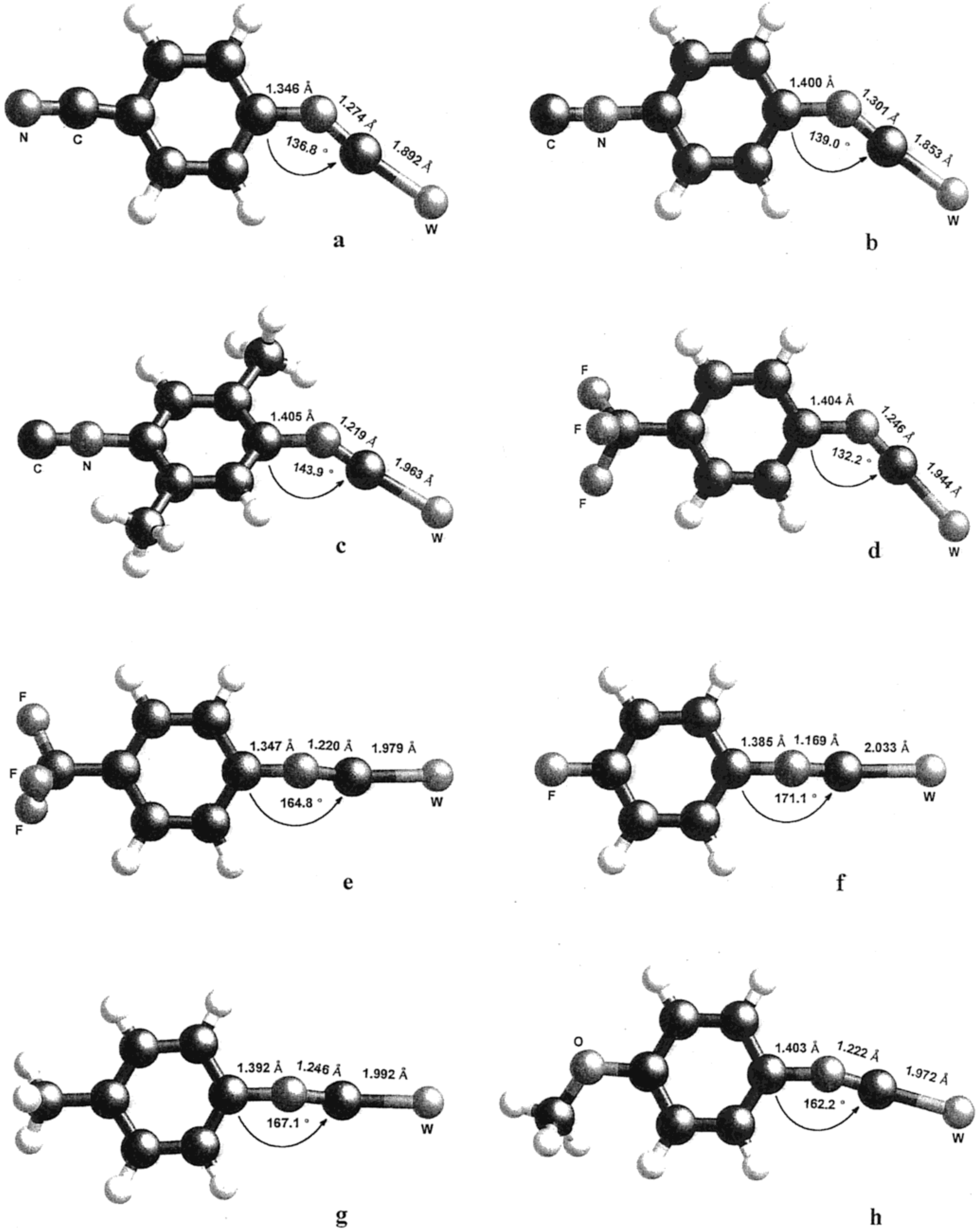

Figure 3. Structures of the isocyanide ligands in (a) (p-NCC$_6$H$_4$NC)$_2$W(dppe)$_2$, (b) (p-CNC$_6$H$_4$NC)$_2$W(dppe)$_2$, (c) (p-CNC$_6$H$_2$(CH$_3$)$_2$NC)$_2$W(dppe)$_2$, (d) and (e) (p-F$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$, (f) (p-FC$_6$H$_4$NC)$_2$W(dppe)$_2$, (g) (p-H$_3$CC$_6$H$_4$NC)$_2$W(dppe)$_2$, and (h) (p-H$_3$COC$_6$H$_4$NC)$_2$W(dppe)$_2$.

teristic patterns which allow for the rapid determination of the conformation of a specific complex. The assignment of conformations by infrared spectroscopy (discussed in more detail below) again indicates that the ligand LUMO energies are effective predictors of these conformations. In addition, the differences in the isocyanide stretching frequencies of the cis versus trans complexes provide insight into their contrasting electron distributions and bonding.

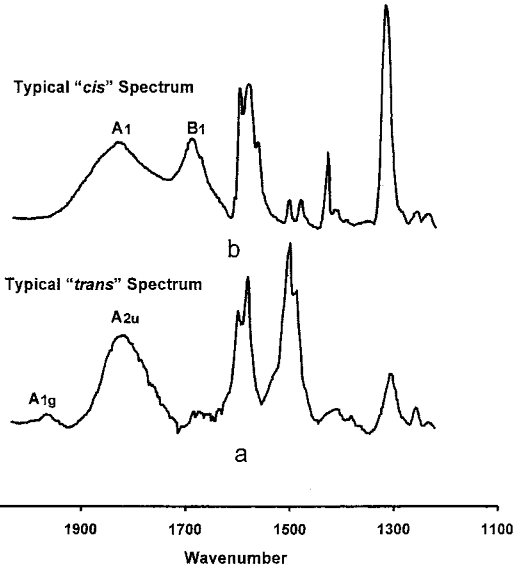

Figure 4. Typical infrared spectra illustrating the patterns for the CN stretching bands in (a) *trans*-(p-$RC_6H_n(CH_3)_{4-n}NC)_2W(dppe)_2$ and (b) *cis*-(p-$RC_6H_n(CH_3)_{4-n}NC)_2W(dppe)_2$.

The isocyanide ligands in both cis and trans complexes experience significant decreases in their CN stretching frequencies upon coordination to the electron-rich tungsten center, which contains six relatively strong σ donors in the coordination sphere: four phosphines and two isocyanides (much better σ donors than CO). These complexes approximate AB_4X_2 structures, where A represents tungsten, B represents the phosphines of dppe, and X represents p-RC_6H_4NC. If the phosphines and isocyanides are treated as point ligands they would be expected to adopt local D_{4h} symmetry with the isocyanide ligands trans to one another and local C_{2v} symmetry with the isocyanides cis to one another. The D_{4h} structure would exhibit two CN stretching modes, a symmetric A_{1g} mode (IR inactive), and an asymmetric A_{2u} (IR active) mode. In a manner similar to CO, the coupling constant for the stretching of two CN groups would be expected to be positive, and the symmetric stretching band would be expected to occur at a higher frequency than the asymmetric band. Figure 4a is an infrared spectrum representative of the *trans* complexes in the CN stretching region. The band at higher frequency is assigned to the in-phase ("symmetric") vibration, which is observable at low intensity because the local symmetry deviates from ideality (allowing a small change in the dipole moment) in the 1940−1980 cm^{-1} region. The out-of-phase ("asymmetric") stretching mode is IR active and observed as a strong band in the 1815−1870 cm^{-1} region. The ideal C_{2v} structure would also exhibit two CN stretching modes, a symmetric A_1 mode, and an asymmetric B_1 mode, both IR active. Figure 4b illustrates the infrared spectrum of a typical cis complex in the CN stretching region. Two medium intensity bands are typically observed, a band due to the in-phase vibration in the 1740−1840 cm^{-1} region and a band resulting from the out-of-phase vibration in the 1650−1700 cm^{-1} region. These patterns are qualitatively very different and provide a simple and rapid means of assessing whether a given complex is in the cis or trans conformation. Importantly, the CN stretching frequencies for the cis complexes occur at substantially lower energies than those for the trans complexes, indicating the decreased bond order effected by the greater back-donation from the metal.

Table 5. Isocyanide Stretching Frequencies for the Complexes *cis*- and *trans*-(p-R-$C_6H_4NC)_2W(dppe)_2$^{a}

isocyanide ligand	configur-ation	ν_{CN} (coordinated)^b	$\Delta\nu_{CN}{}^{b,c}$
p-O_2N-C_6H_4NC:	cis	1743 m, 1662 m	388 sym, 469 asym
p-CN-C_6H_4CN:	cis	1772 m, 1669 m	359 sym, 462 asym
p-CN-C_6H_4NC:	cis	1761 m, 1662 m	370 sym, 469 asym
p-F-C_6H_4NC:	trans	1970 w, 1865 s, br	161 sym, 266 asym
p-F_3C-C_6H_4NC:	cis	1834 m, 1693 m	297 sym, 438 asym
p-CN-$C_6(CH_3)_4NC$:	trans	1943 w, 1819 s, br	188 sym, 312 asym
p-H_3C-C_6H_4NC:	trans	1952 w, 1873 s, br	175 sym, 254 asym
p-H_3CO-C_6H_4NC:	trans	1951 w, 1822 s, br	176 sym, 305 asym

^{a} KBr pellets. ^{b} m = medium, s = strong, br = broad, w = weak, sym = symmetric, asym = asymmetric (for ideally local D_{4h} or C_{2v} symmetry). ^{c} ν_{CN} of the free ligand subtracted from the ν_{CN} of the complex.

Table 6. Electronic Transitions in the Complexes (p-R-$C_6H_4NC)_2W(dppe)_2$

isocyanide ligand	geometry of complex	energy $\pi \rightarrow \pi^*$, nm/cm^{-1}	energy W → P, nm/cm^{-1}	energy W → CN, nm/cm^{-1}
p-CN-C_6H_4NC:	cis	320/31 250	374/26 730	438/22 830
p-F_3C-C_6H_4NC:	cis	323/30 960	366/27 320	431/23 200
p-F-C_6H_4NC:	trans	322/31 060	382/26 180	466/21 460
p-H_3C-C_6H_4NC:	trans	306/32 680	386/25 000	470/21 280
p-H_3CO-C_6H_4NC:	trans	316/31 650	382/26 180	466/21 460

Table 5 summarizes the data for the complexes in this study. As discussed above, adding two methyl groups to the aromatic ring of the diisocyanide ligands failed to increase steric repulsions and/or decrease ligand π acidity sufficiently to keep the ligands from adopting *cis* coordination.

V. Electronic Spectroscopy. The electronic spectra of complexes containing dppe and aromatic isocyanides characteristically exhibit three broad absorption bands. While the maxima in these spectra could not always be resolved, Table 6 summarizes the data for the complexes in the study when absorbances could be resolved. The highest energy absorptions (32 680−30 960 cm^{-1}) result from $\pi - \pi^*$ transitions in the dppe phenyl rings. Free dppe exhibits an absorption maximum at approximately 30 270 cm^{-1} due to this transition. Absorbances in the 27 320−25 000 cm^{-1} region are assigned to tungsten−phosphorus charge-transfer transitions (MLCT), based on the electronic spectrum of the reactant complex *trans*-$(N_2)_2W(dppe)_2$, which exhibits a transition at 366 nm (27 170 cm^{-1}). The absorbances in the 23 200 and 21 280 cm^{-1} region, present only in the isocyanide−phosphine complexes, are assigned as tungsten-to-isocyanide MLCT bands. Similar electronic transition assignments were made for the complexes *trans*-$M(CNR)_2(dppe)_2$ by Richards and Pombeiro[22] (M = Mo or W, R = H_3C, Bu^t, or $H_3CC_6H_5$). A comparison of the spectra for cis and trans complexes proves to be revealing. The tungsten to phosphorus MLTC transitions for the cis complexes are, on the average, over 1000 cm^{-1} higher than those in the trans complexes, while the tungsten to isocyanide transitions are, on the average, 1500 cm^{-1} higher in energy in the cis complexes. This is entirely consistent with the net increase in electronic stabilization effected by strong π acids in the cis complexes, as illustrated qualitatively in Figure 5. The HOMO consists largely of occupied tungsten dπ orbitals and the LUMO is comprised of isocyanide pπ^* orbitals; the lowest virtual orbital with substantial contributions from phosphorus is chiefly phosphorus dπ in character. Considering ligand and tungsten/phosphine frontier orbitals, the formation of the trans complexes, accompanied by moderate back-donation onto the isocyanides,

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[22] Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1979**, *179*, 459.

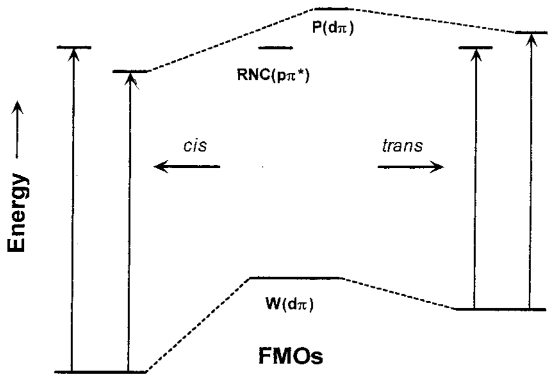

Figure 5. Depiction of relative metal to ligand charge transfer transition energies in *cis*- and *trans*-$(p\text{-}RC_6H_n(CH_3)_{4-n}NC)_2W(dppe)_2$.

lowers the electron−electron repulsion modestly at the metal and slightly on the phosphorus atoms; electron−electron repulsion remains approximately the same in the isocyanide ligands (charge polarization out of the σ FMO is balanced by polarization into the ligand π^* orbitals). The formation of the cis complexes polarizes significant charge into the isocyanide ligands, however, and lowers repulsion substantially on the metal and modestly on the phosphorus atoms.

VI. Mass Spectrometry. Complexes **1**−**8** were characterized using LSIMS. All of the complexes exhibited parent ion peaks at mass-to-charge ratios corresponding to the $[RC_6H_4NC)_2W(dppe)_2]^+$ ions. Measured and calculated isotope ratios for all complexes produced identical matches. Interestingly the trans isomers produced $[W\text{-}dppe]^+$ and $[RC_6H_4NC\text{-}W]^+$ fragments whereas the cis isomers did not. This provides still another indication of the increased metal−ligand bond strength in the electronically stabilized cis complexes.

VII. Creation of a Thermodynamically Stable Trans Diisocyanide Complex. The studies described above indicate clearly that the energies of the lowest energy virtual orbitals on the ligands serve as a reliable guide toward the design of ligands which will produce trans diisocyanide complexes, the target compounds in this research. Based on the spectroscopic and computational studies described, it appeared that a reasonable strategy for the formation of the target trans diisocyanide complexes was modification of the ligands in the *ortho* and *meta* positions, thus forcing the ligand to favor a trans conformation. Addition of two electron-donating methyl groups to the aromatic ring, to increase the steric repulsions of the ligand while simultaneously raising the energy of its LUMO, still failed to produce the trans complex. However, the elevation of the LUMO energy of the ligand attained by adding a single pair of methyl substituents implied that the addition of a second pair of methyl substituents might further increase the energy of the LUMO. The subsequent decrease in electronic stabilization of the complex, coupled with the increased steric effects, could be enough to shift the electronic/steric balance toward the trans conformer. The complex was synthesized and characterized spectroscopically; unfortunately, we were unable to obtain adequate single crystals for X-ray structural analysis. The LSIMS spectrum displayed a parent ion peak at $m/z = 1349$, representing the +1 monomeric product. The isotopic distribution ratios were fully consistent with the stoichiometry of the expected product, $C_{76}H_{72}N_4P_4W$. Spectroscopic data for the complex, $(CNC_6(CH_3)_4NC)W(dppe)_2$, demonstrate convincingly that it has adopted the *trans* conformation in both the solution and the solid state. In solution, the ^{31}P NMR spectrum exhibited a single resonance at 45.5 ppm (downfield from H_3PO_4) with a tungsten−phosphorus coupling constant of 321 Hz. As discussed above, and illustrated in Table 4, this spectrum is characteristic of four chemical shift equivalent phosphorus atoms, all lying on the equatorial plane of a pseudo-octahedral complex, placing the isocyanide ligands trans to one another. The solid-state infrared spectrum exhibited a strong, broad band at 1819 cm^{-1} (shifted 312 cm^{-1} from the free ligand CN stretching frequency), a weak band at 1943 cm^{-1} (shifted 188 cm^{-1}), and a band of moderate intensity at 2114 cm^{-1} (shifted 3 cm^{-1}). The bands at 1943 cm^{-1} (w) and 1819 cm^{-1} (s) correspond to the symmetric and "asymmetric" CN stretching frequencies of coordinated NC; the 2114 cm^{-1} (m) band is due the uncoordinated end of the ligand. Comparison with other complexes of known geometry (Table 5) indicates that the complex also adopts the trans conformation in the solid state. *Thus, manipulation of the energy of the ligand LUMO, as predicted by the model put forth in this work, has resulted in the synthesis of the trans diisocyanide complex sought at the inception of this research.*

When the complex was formed from $(dppe)_2W(N_2)_2$ and $CNC_6(CH_3)_4NC$ in THF under visible light, the monomeric product is obtained almost exclusively. Under more vigorous conditions higher oligomers began to form. The LSIMS spectrum of a product mixture formed in refluxing THF for 48 h exhibited a peak at $m/z = 2512$, consistent with a dimeric product, $(CNC_6(CH_3)_4NC)_3(W(dppe)_2)_2$, a peak at $m/z = 1840$ due to the 2+ cation of the trimer, $(CNC_6(CH_3)_4NC)_4(W(dppe))_3$, and a signal at $m/z = 1614$ due to the 3+ cation of a tetramer, $(CNC_6(CH_3)_4NC)_5(W(dppe)_2)_4$. The infrared spectrum of the product mixture exhibited a strong band at 1826 cm^{-1} (shifted 305 cm^{-1} from the free ligand), a weak band at 1966 cm^{-1} (shifted 165 cm^{-1}), and a peak at 2107 cm^{-1}, characteristic of the uncoordinated isocyanide termini. Comparison with the data in Table 5 indicates that these oligomers adopt the trans conformation at the metal centers, as observed previously in $(CNC_6H_4NC)_{n+1}(W(dppe)_2)_n$.[3]

2. Mechanistic Considerations. I. Dissociative Reaction Scheme. When CNC_6H_4NC and $(N_2)_2W(dppe)_2$ are allowed to react under conditions where the monometallic complex $(CNC_6H_4NC)_2W(dppe)_2$ is formed, the cis product is observed exclusively. However, when a large excess of the bridging isocyanide ligand is present, oligomers are formed which adopt the trans conformation. This suggests that the initial reaction produces trans conformers, which undergo cis to trans interconversion in cases where the cis conformer is more stable, unless they are precluded from doing so with the addition of bulky $W(dppe)_2$ groups, as in the case of oligomer formation. Based on literature precedent, the reaction scenario shown in Scheme 1 would appear to be the most logical for monomer formation. The initial step, the dissociation of N_2, has been proposed by a number of investigators as the first step in ligand displacement in $(N_2)_2M(dppe)_2$, M = Mo or W.[23,24] As in most SN_1 processes, this would be expected to be a relatively slow step. The resulting 5-coordinate complex would then undergo a relatively rapid reaction with RNC, followed by a second slow dinitrogen dissociation and a more rapid ligand addition to form an intermediate trans conformer. In cases where the cis conformer is more stable, a relatively rapid trans to cis interconversion would complete the process. Both dinitrogen

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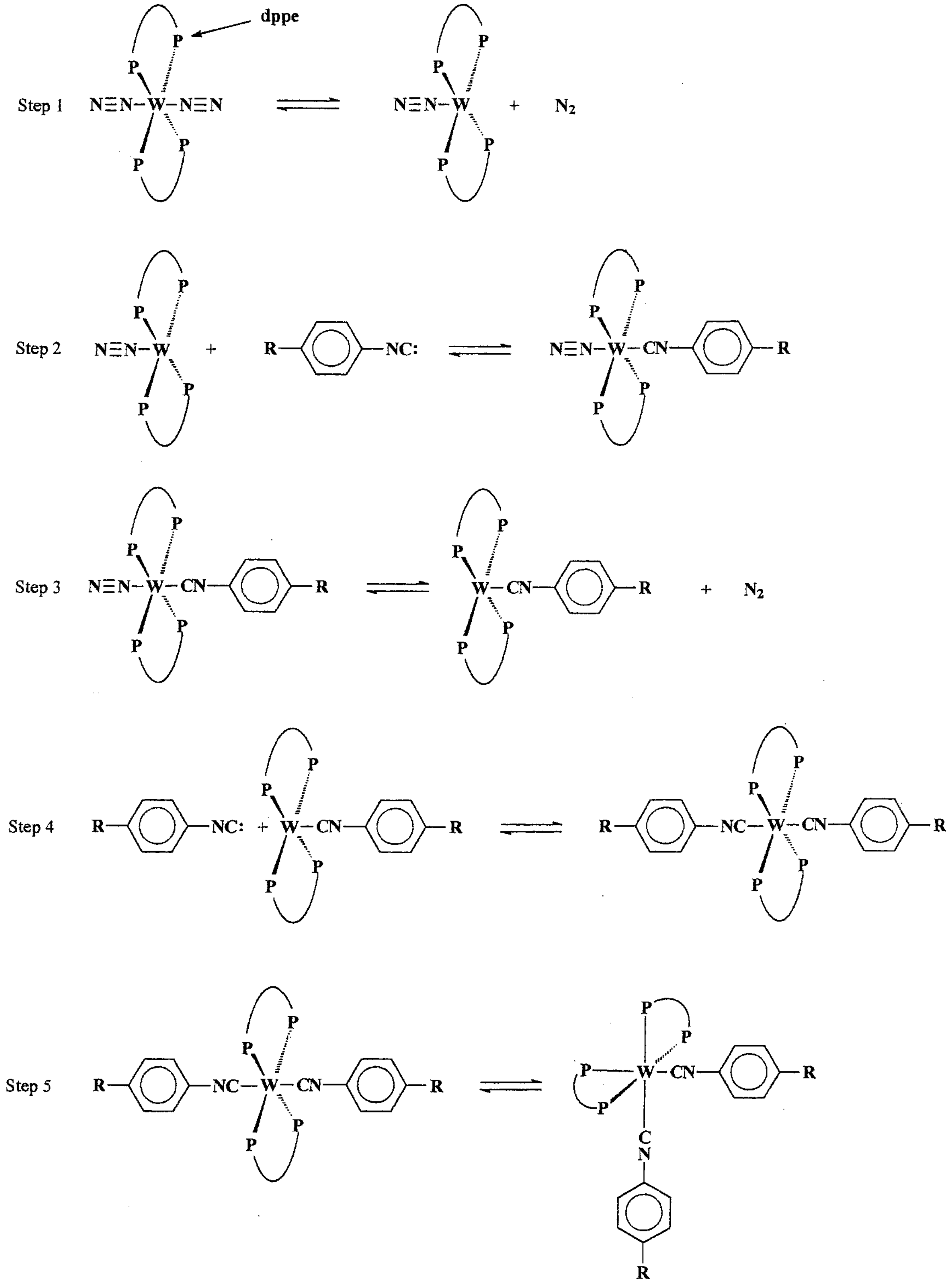
[23] Caruana, A.; Hermann, H.; Kisch, H. *J. Organomet. Chem.* **1980**, *187*, 349. Maples, P. K.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1971**, *10*, 765. Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. *J. Chem. Soc., Dalton Trans.* **1978**, 1638. Carter, L. J.; Bercaw, J. E.; Gray, H. B. *J. Organomet. Chem.* **1979**, *181*, 105.

[24] Pombeiro, A. J. L.; Pickett, J.; Richards, R. L.; Sangokoya, S. A. *J. Organomet. Chem.* **1980**, *202*, C15.

Scheme 1. Proposed Dissociative Mechanism for the Formation of (p-$RC_6H_n(CH_3)_{4-n}NC)_2W(dppe)_2$



dissociations would be expected to be preequilibria under a nitrogen atmosphere, and one of them should be the rate-limiting step. The complexes undergoing dissociation in this scheme differ only in that an isocyanide ligand has formally replaced a dinitrogen ligand; the relative rates of these two potential rate-limiting steps depend on whether the second $W-N_2$ bond is strengthened or weakened when RNC replaces N_2.

If the second dissociation (step 3) is rate-limiting, it should be possible to identify the monosubstituted intermediate, since the time scale of the reaction is several hours. There is a large literature precedent for molybdenum-containing analogues of this putative intermediate;[24,25] surprisingly, there are no known tungsten−phosphine complexes containing a single dinitrogen and a π-acidic ligand. Under "normal" reaction conditions, no evidence (^{31}P NMR, IR, LSIMS) for a monosubstituted intermediate was observed. Even under more stringent conditions at 273 K, where it takes several days to observe small amounts of product via ^{31}P NMR, no additional resonances were observed, strongly suggesting that the intermediate *trans*-$(N_2)(p$-$CNC_6H_4NC)W(dppe)_2$ (or any other intermediate) is

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(25) Tatsumi, T.; Hidai, M.; Uchida, T. *Inorg. Chem.* **1975**, *14*, 2530. Pombeiro, A. J. L. *Inorg. Chim. Acta* **1992**, *198*, 179.

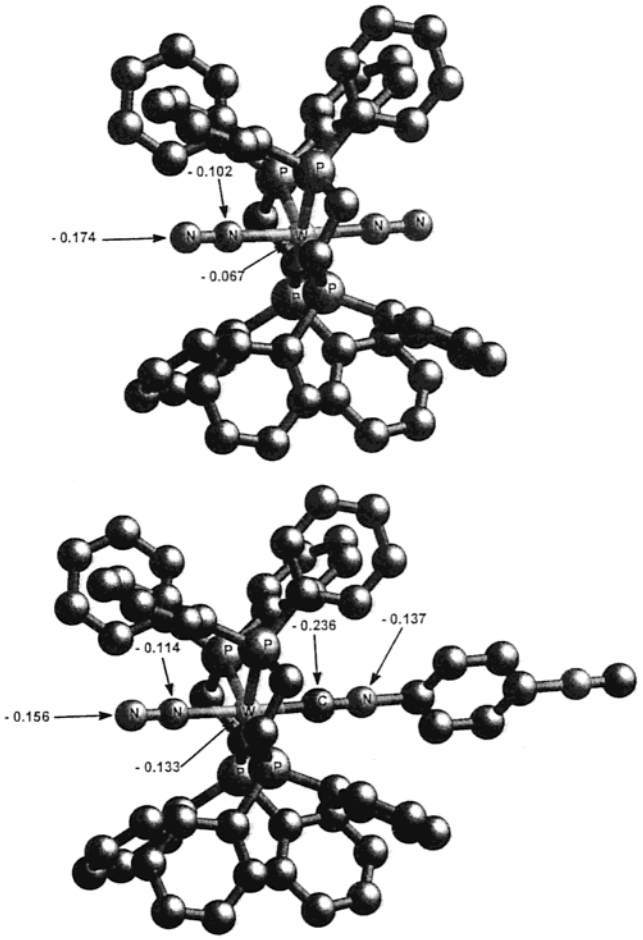

Figure 6. Calculated atomic charges (DFT: BECKE3LYP/LANL2DZP) on W, N_2, and CN in *trans*-$(N_2)_2W(dppe)_2$ and *trans*-$N_2(CNC_6H_4NC)W(dppe)_2$.

kinetically labile. Although, as mentioned earlier, a number of monosubstituted molybdenum analogues of this proposed intermediate have been reported,[24−26] the reaction between *trans*-$(N_2)_2Mo(dppe)_2$ and *p*-CNC_6H_4NC also produced only *cis*-(*p*-$CNC_6H_4NC)_2Mo(dppe)_2$.

The infrared spectra of the dinitrogen stretching frequencies in the series of complexes *trans*-$Mo(L)(N_2)(dppe)_2$ provide support for the premise that the second dissociation would not be rate-limiting. For L = C_6H_5CN:, N_2, C_6H_5NC:, and CO, the N_2 stretching frequencies are 1945, 1970, 2049, and 2128 cm^{-1}, respectively.[26] This indicates that an aromatic isocyanide, a stronger π acid than dinitrogen, polarizes charge away from N_2 toward the isocyanide ligand, even though the isocyanide ligand is a stronger base. Consequently, the N≡N bond strengthens and the M−N bond weakens. Thus the metal nitrogen bond is weakened when ArNC is substituted for N_2, and it would be suspected that the S_N1 displacement would occur more rapidly. Density functional calculations comparing *trans*-$(N_2)_2W(dppe)_2$ with *trans*-(N_2)(*p*-$CNC_6H_4NC)W(dppe)_2$ lend credence to this thesis. Figure 6 shows calculated atomic charges on the atoms which are the major participants in metal−ligand π bonding for these two complexes. Upon replacement of a dinitrogen ligand with *p*-CNC_6H_4NC, electron density on the tungsten center increases, while the net charge density on the dinitrogen ligand decreases slightly. The terminal nitrogen atom experiences a loss in charge density, while the coordinated nitrogen atom becomes more negative. The charge product (q_1q_2) for the nitrogen atoms remains constant (0.018), indicating that the electrostatic component to the bond does not change, while the covalent component increases; the N−N bond becomes stronger. The charge product for the W−N pair doubles (from 0.007 to 0.015), resulting in increased repulsion between the atoms and a weakening of the bond. A more facile dissociation would be expected.

Based on the above discussion, the first dissociation of dinitrogen would be expected to be the rate-limiting step in the proposed reaction scheme. Under a nitrogen atmosphere the first dissociation would be expected to be a preequilibrium process, and shifting the equilibrium should therefore increase the reaction rate, provided that the second step did not occur more rapidly than the recoordination of N_2 (an unlikely scenario since the isocyanide ligand is much larger than dinitrogen). A simple, yet rigorous experiment was conducted to test whether *either* dinitrogen dissociation step is rate-limiting. The reaction was performed under an argon atmosphere with a constant argon purge while monitoring the reaction rate. *Surprisingly, no increase in the rate was observed!*

Moreover, the observation that the reaction rate was considerably decreased (by a factor of 5) when toluene was substituted for THF as the reaction solvent was puzzling, since this clearly should not be the case if the rate-limiting step is dissociative in nature. In addition, the slower reaction in toluene, monitored by ^{31}P NMR, revealed the presence of a reaction intermediate not observed in the faster reaction in THF. LSIMS mass spectra revealed no ion characteristic of the monosubstituted intermediate discussed above, and infrared spectra exhibited only a single dinitrogen stretching frequency due to the starting material. As previously indicated, the monosubstituted intermediate would be expected to have a noticeably higher stretching frequency than the bis-dinitrogen complex; none was observed. The ^{31}P resonance due to the intermediate was observed at 50.6 ppm. The peak was broad, but it sharpened as the temperature was lowered and eventually disappeared as the reaction progressed. This resonance was essentially identical to ^{31}P spectra of the trans complexes described in Part I (Table 4) and hinted that the mechanism might involve the initial formation of a trans complex undergoing dynamic phosphine exchange.

II. Associative Reaction Scheme. Scheme 2 presents a reaction scenario which is consistent with the observations cited above. We have observed dppe ring opening in other studies involving tungsten-dppe complexes,[27] and it has been observed in other reaction mechanisms.[28] For example, Basallotte et al.[29] were faced with a similar dilemma in describing the substitution of dihydrogen with NCMe, NCC_6H_5, or DMSO in *trans*-$[FeH(H_2)(dppe)_2]^+$. The reaction kinetics were inconsistent with an H_2 dissociation step but were consistent with a chelating phosphine becoming monodentate with a weakly coordinated solvent molecule occupying the open coordination site, followed by associative ligand attack, coupled with loss of hydrogen and recoordination of the "dangling" phosphorus atom. The broad ^{31}P resonance for all the trans complexes, which sharpens (reversibly) upon cooling, is strong evidence that dppe ring opening and closing is occurring dynamically, on the NMR time

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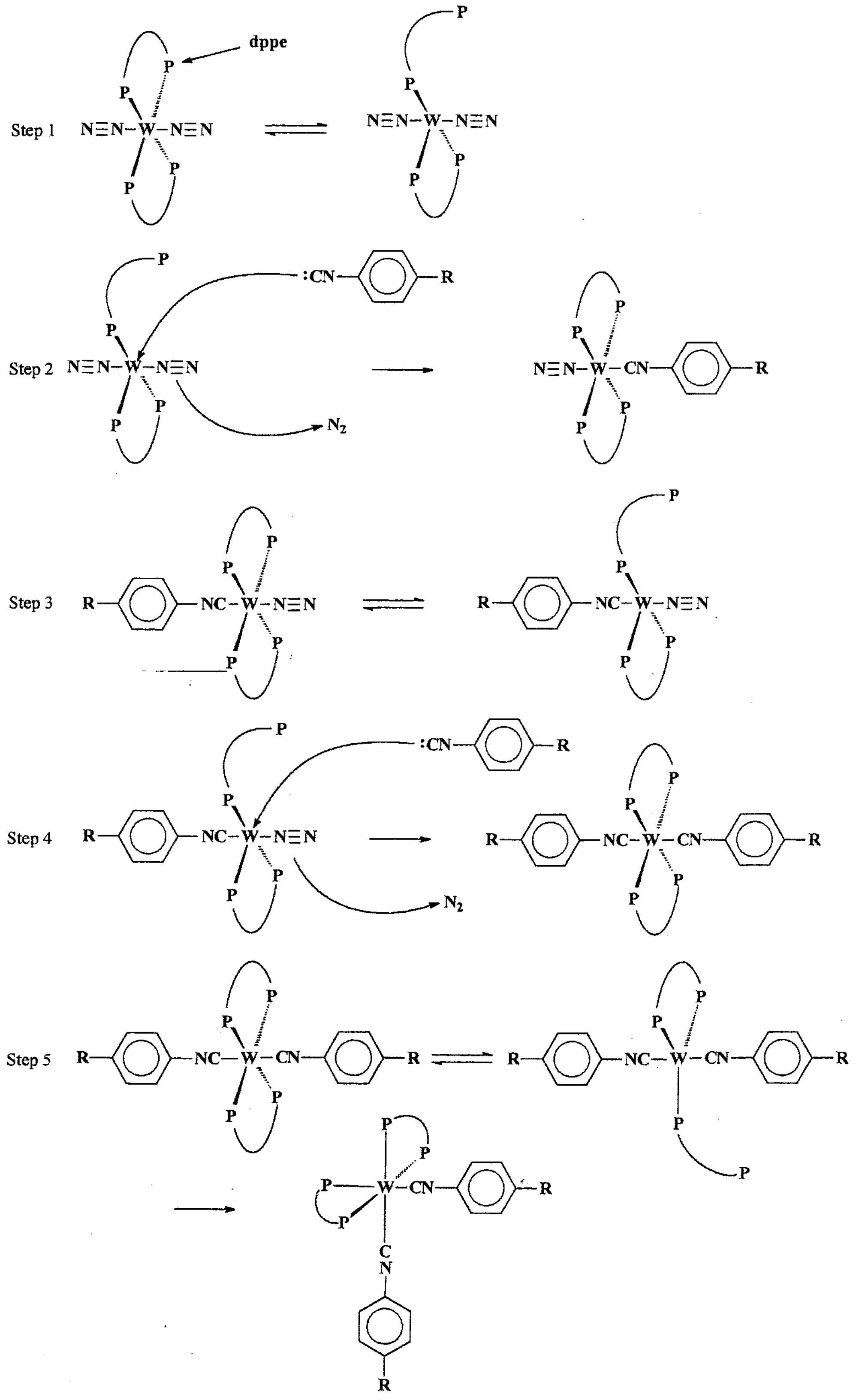
[26] Nakamura, G.; Harada, Y.; Arita, C.; Seino, H.; Mizobe, Y.; Hidai, M. *Organometallics* **1998**, *17*, 1010.

[27] Hodgeman, W. C. *Part 2: An Investigation Into the Chemistry of Low-valent Tungsten-Phosphine Complexes in the Presence of $WOCl_4$.*, Doctoral Dissertation, University of Wisconsin-Milwaukee, 1997.

[28] Robinson, W. R.; Wigley, D. E.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 918.

[29] Basallote, M. G.; Durán, J.; Fernández-Trujillo, M. J.; González, G.; Máñez, M. A.; Martinez, M. *Inorg. Chem.* **1998**, *37*, 1623.

Scheme 2. Proposed Associative Mechanism for the Formation of (p-$RC_6H_n(CH_3)_{4-n}NC)_2W(dppe)_2$



scale. The initial steps (steps 1 and 2), analogous to those proposed by Basalotte, are consistent with these observations. The faster reaction rate in THF is probably due to weak solvent coordination and stabilization of the intermediate produced in step 1. Since the coordination of the first isocyanide ligand weakens the W−N bond to the second dinitrogen ligand, the third step could either undergo a rapid dinitrogen dissociation followed by ligand attack or a second ring opening, followed by associative displacement (steps 3 and 4). The resulting trans complex could then either undergo conversion to the cis conformer in the event that it is thermodynamically more stable or remain *trans.* While the interconversion could proceed via a Bailar twist mechanism,[30] rearrangement of the five coordinate, monodentate species seems more likely (as shown in step 5).

III. Creation of a Kinetically Robust Trans Diisocyanide Complex. If the second reaction scheme is reasonable, the rate-limiting step is likely to be the initial phosphorus atom dissociation in step 1. To test this hypothesis we sought a way to impede this first step and determine its affects on the reaction rate. In examining the reaction of RMo(CO)$_3$C$_5$H$_5$ (R = CH$_3$ or C$_6$H$_5$CH$_2$) with bidentate phosphine ligands, King and coworkers discovered that dppe (1,2-bis(diphenylphosphino)-ethane) was able to bridge two metal centers to form (dppe)-[Mo(CO)$_2$(COR)(C$_5$H$_5$)]$_2$, while dppee (*cis*-1,2-bis(diphenylphosphino)ethene) was unable to do so, forming only the monometallic complex, (dppee)Mo(CO)$_2$.[31] King attributed the inability of dppee to act as a bridging ligand to the rigidity of the ethylene group, which would constrain the phosphorus atoms to a single metal center. The free rotation of the ethane moiety in dppe would permit it to reduce steric repulsions between Mo fragments, allowing for the formation of the bimetallic complex. Based upon this premise, we expected the rate of phosphine exchange to be reduced significantly by substituting dppee for dppe in the reactions under investigation, since the "dissociated" phosphine should remain in the proximity of the tungsten center, rather than rotating away as a "dangling" atom. If, as expected, the initial dppe ring opening is rate-limiting, the substitution should result in a slower reaction. The results of this substitution were dramatic. The reaction between *trans*-(N$_2$)$_2$W(dppe)$_2$ and *p*-CNC$_6$H$_4$NC was complete in 48 h, while the reaction between *trans*-(N$_2$)$_2$W(dppee)$_2$ and *p*-CNC$_6$H$_4$NC was only 30% complete (based on formation of the cis complex) after the same period. After a 48 h period the ^{31}P NMR spectrum of the latter reaction mixture exhibited two sharp doublets of equal intensity (relative intensity of each doublet = 34) at 49.8 ppm (J_{pp} = 5.6 Hz) and 55.5 ppm (J_{pp} = 5.6 Hz), corresponding to *cis*-(*p*-CNC$_6$H$_4$NC)$_2$W(dppee)$_2$, a sharp peak at 61.1 ppm (relative intensity = 100) from *trans*-(N$_2$)$_2$W(dppee)$_2$, and a broader resonance at 61.9 ppm (relative intensity = 56) corresponding to *trans*-(*p*-CNC$_6$H$_4$NC)$_2$W(dppee)$_2$. Although the *trans* complexes have two magnetically inequivalent phosphorus nuclei, the coupling constants were too small to be resolved. The dppee ligand slowed the reaction to a point where accumulation of the trans diisocyanide complex was observed. This strongly indicates that the trans to cis interconversion proceeds by a ring opening process, since the rate of interconversion is retarded significantly when dppe is replaced with dppee. After 48 h the trans to cis ratio is close to 1:1, indicating that it may be possible to create and trap trans conformers, storing them at low temperatures. Previous results in our laboratory indicate that further reaction of these monomeric species to produce oligomers will "lock-in" the *trans* conformation.[3]

Conclusions

Based on these studies, it is evident that the *para* substituents on the isocyanide ligands in (*p*-RC$_6$H$_4$NC)$_2$W(dppe)$_2$ have a pronounced effect on the electronic stabilization of the complexes. In cases where the substituents are electron-withdrawing, the ligands tend to behave as stronger π acids, and the cis conformation is preferred thermodynamically. As the substituents become electron-donating, and consequently weaker π acids, the steric repulsions of the large aryl phosphine ligands come into play. The result is a preference for the trans conformer with isocyanide ligands that are incapable of polarizing enough charge density away from the metal to provide the electronic stabilization necessary for the adoption of the less sterically favorable cis conformation. Thus, replacement of the hydrogen atoms with methyl groups at the *ortho* and *meta* positions of the aromatic ring increased the steric bulk of the diisocyanide bridging ligand and simultaneously decreased its π acidity. The result was the formation of a new, thermodynamically stable trans diisocyanide complex.

The formation and conformational transformation of the diisocyanide complexes appear to proceed via a ligand association mechanism, where ligand displacement in each step is preceded by a single phosphorus atom of a bidentate phosphine ligand leaving the coordination sphere, opening up a site for ligand attack. This process was retarded significantly by constraining free rotation about the P−R−P link in the bidentate phosphine with a double bond, keeping the phosphorus atom in the coordination environment. This constraint decreased the rate of reaction sufficiently to enable the observation of a trans intermediate in the reaction scheme, a kinetically robust trans diisocyanide complex. In summary, these studies have provided the means to prepare either thermodynamically stable or kinetically trapped trans diisocyanide complexes of tungsten containing bulky bidentate aryl phosphine ligands.

Acknowledgment. We thank Professor Robin Rogers at the University of Alabama for collecting X-ray diffraction data on three of the crystals in this study. We are also indebted to our colleagues in the Department of Chemistry at UWM for their continued support of this research.

Supporting Information Available: Tables of atomic coordinates and anisotropic thermal parameters for **2**, **4**, **5**, **6**, and **7** (PDF). This material is available free of charge via the Internet at http://pbs.acs.org.

JA0018466

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(30) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.

(31) King, R. B.; Houk, L. W.; Kapoor, P. N. *Inorg. Chim. Acta* **1968**, *2*, 1792.