

Comparison of the Relative Electron-Donating Abilities of Hydridotris(pyrazolyl)borate and Cyclopentadienyl Ligands: Different Interactions with Different Transition Metals

Sir: The hydridotris(pyrazolyl)borate (Tp) ligand has proven to be a versatile ancillary group.^{1–8} Complexes of the Tp ligand (or one of its substituted derivatives) with every transition metal have been prepared. The Tp ligand is frequently used as an analogue of cyclopentadienyl (Cp) because of its ability to serve as a facially coordinating, anionic six-electron donor (Figure 1).

In general, the sterically encumbering nature of the Tp ligand is the primary reason for its utilization in place of the Cp ligand. These steric constraints dominate observed reactivity patterns, frequently permitting the isolation of molecules whose Cp relatives are highly reactive.^{3,9} With this in mind we decided to prepare hydridotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) ligand analogues of our Cp*Ir(III) systems and investigate their ability to activate C–H bonds.¹⁰ Unexpectedly, these complexes were not as reactive as their Cp* analogues, which led us to conclude that the Cp* ligand was substantially more electron donating than the Tp^{Me2} ligand as a result of an electronic effect imposed by the Tp^{Me2} ligand.¹¹ In a search for precedent, a survey of the literature revealed different and sometimes conflicting reports on the relative electron-donating properties of the Cp and Tp ligands toward different metals.^{12–14} This discrepancy has prompted us to put forth in this paper a brief summary of the data germane to this topic.¹⁵

Table 1 summarizes literature data regarding the electronic properties of transition metals possessing the Tp/Tp^{Me2} and Cp/Cp* ligands.¹⁶ We have focused primarily on comparing infrared and, if available, electrochemical data, both of which reflect the relative elec-

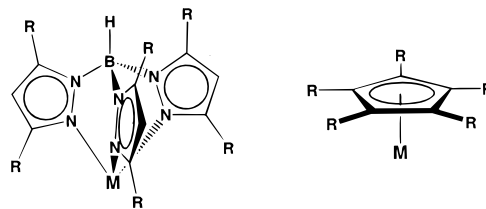


Figure 1. Hydridotris(pyrazolyl)borate ligand and cyclopentadienyl ligand. Cone angle for Cp = 150° (R = H), 182° (R = Me) and Tp = 262° (R = H), 276° (R = Me).³

tronic properties at the metal center most accurately.^{17,18} Where IR and electrochemical measurements are unavailable, data obtained with alternate techniques (e.g., NMR spectroscopy, X-ray crystallographic data, metal-acidity measurements) have been summarized.

Groups 4 and 5. Data for group 4 and 5 Cp and Tp complexes are relatively limited. For titanium, the Cp and Cp* ligands are apparently more donating than Tp^{Me2}, as evidenced by the differences in ¹³C NMR chemical shifts of the quaternary and methyl carbons of an ancillary imido ligand (Table 1).^{19–21} In contrast, the Tp ligand is a better electron donor than the Cp ligand toward vanadium.^{22,23} The shorter metal–imido vanadium–nitrogen bond length in Cp(Cl)₂V=NBu^t, compared with Tp(Cl)₂V=NBu^t, is described in terms of a more electrophilic metal center, thereby resulting in a tighter anion (ligand)/cation (metal) pair.¹³ An NMR analysis similar to that utilized for titanium demonstrated that Cp and Tp^{Me2} have similar donating abilities toward tantalum (Table 1).^{24,25}

Groups 6 and 7. The variable electron-donating capabilities of these two ligand classes is clearly demonstrated by data from groups 6 and 7. A thorough electrochemical and infrared examination of the group 6 metal carbonyl complexes of the type LM(CO)₃[–] (L =

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(10) See: (a) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, 115, 10462–10463. (b) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, 270, 1970–1973.

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(12) A similar discrepancy has been noted. See refs 13 and 14.

(13) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, 16, 4071–4076.

(14) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, 120, 8747–8754.

(15) A summary of the relative electron-donating properties of substituted poly(pyrazolyl)borato ligands can be found in ref 3.

(16) Only the Tp/Tp^{Me2} systems have been examined. These ligands are most frequently used in place of the cyclopentadienyl ligand.

(17) Hunter, A. D.; Mozol, V.; Tsai, S. D. *Organometallics* **1992**, 11, 2251–2262.

(18) A referee has asked us to emphasize that infrared data provide a generally reliable indication of electron density for a metal in one oxidation state, but electrochemical data reflect the relative stability of two adjacent oxidation states and should therefore be interpreted with caution.

(19) Dunn, S. C.; Mountford, P.; Shishkin, O. V. *Inorg. Chem.* **1996**, 35, 1006–1012.

(20) The authors in ref 19 suggest that magnetic anisotropy is unimportant in the comparison of ¹³C NMR chemical shifts.

(21) Infrared data on [TpTi(CO)₄][–] and [Cp*Ti(CO)₄][–] seem to indicate that Cp* and Tp have similar donating properties. These spectra were acquired in different media, and the authors caution that the geometries of the respective “TiCO₄” fragments might be different. See: Chi, K. M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, 110, 163–171.

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Table 1. Summary of the Electron-Donating Properties of Some Transition Metal Cyclopentadienyl and Hydridotris(pyrazolyl)borate Complexes

compound	data	ref
Titanium		
Tp ^{Me} ₂ Ti(NBu ^t)Cl(pyBu ^t)	¹³ C{ ¹ H} NMR (N(C ₆ (CH ₃) ₃) δC _q - δCH ₃ = 38.4 ppm	19
CpTi(NBu ^t)Cl(pyBu ^t)	¹³ C{ ¹ H} NMR (N(C ₆ (CH ₃) ₃) δC _q - δCH ₃ = 37.5 ppm	19
Cp ^{Me} ₂ Ti(NBu ^t)Cl(pyBu ^t)	¹³ C{ ¹ H} NMR (N(C ₆ (CH ₃) ₃) δC _q - δCH ₃ = 36.7 ppm	19
[TpTi(CO) ₄][Et ₄ N]	ν _{CO} = 1912, 1772 cm ⁻¹ (CH ₃ CN)	21
[Cp*Ti(CO) ₄][Et ₄ N]	ν _{CO} = 1914, 1772 cm ⁻¹ (DME)	21
Vanadium		
TpV(NBu ^t)Cl ₂	V=N 1.638(2) Å	22
CpV(NBu ^t)Cl ₂	V=N 1.590(4) Å	23
Tantalum		
Tp ^{Me} ₂ Ta(NBu ^t)Cl ₂	¹³ C{ ¹ H} NMR (N(C ₆ (CH ₃) ₃) δC _q - δCH ₃ = 34.56 ppm	24
CpTa(NBu ^t)Cl ₂	¹³ C{ ¹ H} NMR (N(C ₆ (CH ₃) ₃) δC _q - δCH ₃ = 34.28 ppm	25
Chromium		
[TpCr(CO) ₃][Et ₄ N]	ν _{CO} = 1889, 1751 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.821 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[CpCr(CO) ₃][Et ₄ N]	ν _{CO} = 1888, 1768 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.688 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[Tp ^{Me} ₂ Cr(CO) ₃][Et ₄ N]	ν _{CO} = 1881, 1742 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.857 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
Molybdenum		
[TpMo(CO) ₃][Et ₄ N]	ν _{CO} = 1888, 1752 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.521 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[CpMo(CO) ₃][Et ₄ N]	ν _{CO} = 1891, 1770 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.403 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[Tp ^{Me} ₂ Mo(CO) ₃][Et ₄ N]	ν _{CO} = 1881, 1745 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.583 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
Tp(CO) ₂ Mo(CBu)	ν _{CO} = 1992, 1902 cm ⁻¹ (CH ₂ Cl ₂)	31
Cp(CO) ₂ Mo(CBu)	ν _{CO} = 1992, 1913 cm ⁻¹ (CH ₂ Cl ₂)	31
Cp*MoO ₂ (CH ₃)	ν _{MoO} = 918, 877 cm ⁻¹ (Nujol)	32
Tp ^{Me} ₂ MoO ₂ (CH ₃)	ν _{MoO} = 936, 904 cm ⁻¹ (Nujol)	32
Tungsten		
[TpW(CO) ₃][Et ₄ N]	ν _{CO} = 1886, 1765 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.582 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[CpW(CO) ₃][Et ₄ N]	ν _{CO} = 1889, 1751 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.397 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
[Tp ^{Me} ₂ W(CO) ₃][Et ₄ N]	ν _{CO} = 1872, 1733 cm ⁻¹ (CH ₃ CN) E _{ox} = -0.652 V (M ⁻ /M vs Fc ⁺ /Fc)	26, 27a
Cp*WO ₂ (CH ₃)	ν _{MoO} = 943, 899 cm ⁻¹ (Nujol)	32
Tp ^{Me} ₂ WO ₂ (CH ₃)	ν _{MoO} = 955, 914 cm ⁻¹ (Nujol)	32
Cp*WO ₂ (CH ₂ SiMe ₃)	ν _{MoO} = 937, 901 cm ⁻¹ (Nujol)	32
Tp ^{Me} ₂ WO ₂ (CH ₂ SiMe ₃)	ν _{MoO} = 954, 910 cm ⁻¹ (Nujol)	32
Manganese		
CpMn(CO) ₃	ν _{CO} = 2028, 1947 cm ⁻¹ (hexanes)	27b
Cp*Mn(CO) ₃	ν _{CO} = 2017, 1929 cm ⁻¹ (hexanes)	33
TpMn(CO) ₃	ν _{CO} = 2042, 1941 cm ⁻¹ (hexanes)	34
Tp ^{Me} ₂ Mn(CO) ₃	ν _{CO} = 2032, 1927 cm ⁻¹ (hexanes)	34
Technetium		
TpTc(CO) ₃	ν _{CO} = 2024, 1913 cm ⁻¹ (KBr)	36
Tp ^{Me} ₂ Tc(CO) ₃	ν _{CO} = 2022, 1911 cm ⁻¹ (KBr)	36
Cp*Tc(CO) ₃	ν _{CO} = 2005, 1904 cm ⁻¹ (KBr)	37
Rhenium		
CpRe(CO) ₃	ν _{CO} = 2021, 1926 cm ⁻¹ (THF) ν _{CO} = 2019, 1897 cm ⁻¹ (KBr)	27b
Cp*Re(CO) ₃	ν _{CO} = 2008, 1912 cm ⁻¹ (THF) ν _{CO} = 1999, 1892 cm ⁻¹ (KBr)	27b
TpRe(CO) ₃	ν _{CO} = 2024, 1914 cm ⁻¹ (THF) ν _{CO} = 2020, 1896 cm ⁻¹ (KBr)	38
Tp ^{Me} ₂ Re(CO) ₃	ν _{CO} = 2017, 1893 cm ⁻¹ (KBr)	36
CpRe(CO) ₂ (THF)	ν _{CO} = 1910, 1836 cm ⁻¹ (THF)	39
TpRe(CO) ₂ (THF)	ν _{CO} = 1907, 1823 cm ⁻¹ (THF)	27b
CpRe(CO) ₂ (NH ₃)	ν _{CO} = 1900, 1820 cm ⁻¹ (CH ₂ Cl ₂)	40
TpRe(CO) ₂ (NH ₃)	ν _{CO} = 1883, 1788 cm ⁻¹ (CH ₂ Cl ₂)	27b
Cp*ReO ₃	ν _{ReO} = 1921, 890 cm ⁻¹ (KBr)	41
TpReO ₃	ν _{ReO} = 1944, 908 cm ⁻¹ (CsI)	41
Cp*Re(O)(O ₂ C ₂ H ₄)	ν _{ReO} = 907 cm ⁻¹ (KBr) Re=O 1.696(2) Å	42

Table 1. (Continued)

compound	data	ref
Rhenium TpRe(O)(O ₂ C ₂ H ₄)	$\nu_{\text{ReO}} = 985 \text{ cm}^{-1}$ (Nujol) Re=O 1.654(7) Å	43
Iron Cp ₂ Fe	$E_{\text{ox}} = 0.08 \text{ V}$ (SO ₂ , -40 °C)	44
Cp ₂ *Fe	$E_{\text{ox}} = -0.27 \text{ V}$ (SO ₂ , -40 °C)	44
Tp ₂ Fe	$E_{\text{ox}} = -0.15 \text{ V}$ (SO ₂ , -40 °C)	44
Ruthenium Tp(PPh ₃)Ru(CO)X	$\nu_{\text{CO}} = 1922 \text{ cm}^{-1}$ (Nujol) (X = H) $\nu_{\text{CO}} = 1965 \text{ cm}^{-1}$ (Nujol) (X = Cl) $\nu_{\text{CO}} = 2095, 2033 \text{ cm}^{-1}$ (Nujol) (X = CO ⁺) $\nu_{\text{CO}} = 2021 \text{ cm}^{-1}$ (Nujol) (X = CN ^t Bu) $\nu_{\text{CO}} = 1975 \text{ cm}^{-1}$ (Nujol) (X = PMe ₃ ⁺)	45
Cp(PPh ₃)Ru(CO)X	$\nu_{\text{CO}} = 1931 \text{ cm}^{-1}$ (Nujol) (X = H) $\nu_{\text{CO}} = 1958 \text{ cm}^{-1}$ (Nujol) (X = Cl) $\nu_{\text{CO}} = 2075, 2030 \text{ cm}^{-1}$ (Nujol) (X = CO ⁺) $\nu_{\text{CO}} = 2014 \text{ cm}^{-1}$ (Nujol) (X = CN ^t Bu) $\nu_{\text{CO}} = 1995 \text{ cm}^{-1}$ (Nujol) (X = PMe ₃ ⁺)	45
[TpRu(CO)(dippe)][BPh ₄] dippe = Ph ₂ P(CH ₂) ₂ N(ⁱ Pr) ₂	$\nu_{\text{CO}} = 1973 \text{ cm}^{-1}$ (Nujol)	46
[CpRu(CO)(dippe)][BPh ₄]	$\nu_{\text{CO}} = 1959 \text{ cm}^{-1}$ (Nujol)	46
[Cp*Ru(CO)(dippe)][BPh ₄]	$\nu_{\text{CO}} = 1926 \text{ cm}^{-1}$ (Nujol)	46
[TpRu(N ₂)(dippe)][BPh ₄]	$\nu_{\text{CO}} = 2165 \text{ cm}^{-1}$ (Nujol)	46
[TpRu(N ₂)(dmpe)][BPh ₄] dmpe = Ph ₂ P(CH ₂) ₂ N(Me) ₂	$\nu_{\text{NN}} = 2182 \text{ cm}^{-1}$ (diff reflectance)	47
[CpRu(N ₂)(dipe)]	$\nu_{\text{NN}} = 2145 \text{ cm}^{-1}$ (Nujol)	46
[Cp*Ru(N ₂)(dipe)]	$\nu_{\text{NN}} = 2120 \text{ cm}^{-1}$ (Nujol)	46
Osmium CpOs(N)Ph ₂	$\nu_{\text{OsN}} = 1080 \text{ cm}^{-1}$ (KBr) Os≡N 1.660(9) Å	13
TpMe ₂ Os(N)Ph ₂	$\nu_{\text{OsN}} = 1094 \text{ cm}^{-1}$ (KBr) Os≡N 1.648 (3) Å	13
<i>trans</i> -[CpOsH ₂ (PPh ₃) ₂][BF ₄]	$pK_{\text{a}} = 13.4$ (MH ₂ ⁺) $E_{\text{ox}} = -0.38 \text{ V}$ (M ⁺ /M vs Fc ⁺ /Fc)	48, 27a
[TpOs(H ₂)(PPh ₃) ₂][BF ₄]	$pK_{\text{a}} = 8.9$ (MH ₂ ⁺) $E_{\text{ox}} = -0.22 \text{ V}$ (M ⁺ /M vs Fc ⁺ /Fc)	48, 27a
Rhodium TpRh(CO)I ₂	$\nu_{\text{CO}} = 2112 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	50a
TpMe ₂ Rh(CO)I ₂	$\nu_{\text{CO}} = 2095 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	50b
CpRh(CO)I ₂	$\nu_{\text{CO}} = 2085 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	51, 27b
Cp*Rh(CO)I ₂	$\nu_{\text{CO}} = 2068 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	52, 27b
TpMe ₂ Rh(CO) ₂	$\nu_{\text{CO}} = 2054, 1981 \text{ cm}^{-1}$ (hexanes)	53
CpRh(CO) ₂	$\nu_{\text{CO}} = 2046, 1982 \text{ cm}^{-1}$ (decalin)	54
Cp*Rh(CO) ₂	$\nu_{\text{CO}} = 2026, 1964 \text{ cm}^{-1}$ (hexanes)	55
Iridium TpMe ₂ Ir(CO) ₂	$\nu_{\text{CO}} = 2039, 1960 \text{ cm}^{-1}$ (hexanes)	56
Cp*Ir(CO) ₂	$\nu_{\text{CO}} = 2020, 1953 \text{ cm}^{-1}$ (hexanes)	57
Tp(H) ₂ Ir(CO)	$\nu_{\text{CO}} = 2020 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	58
Cp(H) ₂ Ir(CO)	$\nu_{\text{CO}} = 2002 \text{ cm}^{-1}$ (CH ₂ Cl ₂)	59
TpMe ₂ Ir(C ₂ H ₄)CO	$\nu_{\text{CO}} = 1990 \text{ cm}^{-1}$ (Nujol)	60
TpIr(C ₂ H ₄)CO	$\nu_{\text{CO}} = 2000 \text{ cm}^{-1}$ (cyclohexane)	62
CpIr(C ₂ H ₄)CO	$\nu_{\text{CO}} = 1980 \text{ cm}^{-1}$ (cyclohexane)	63
TpMe ₂ (C ₂ H ₃)Ir(H)CO	$\nu_{\text{CO}} = 2020 \text{ cm}^{-1}$ (petroleum ether)	60
Cp(C ₂ H ₃)Ir(H)CO	$\nu_{\text{CO}} = 2021 \text{ cm}^{-1}$ (CO matrix)	61
[TpMe ₂ (PMe ₃)IrMe(CO)][B(C ₆ H ₃ (CF ₃) ₂) ₄]	$\nu_{\text{CO}} = 2060 \text{ cm}^{-1}$ (KBr)	11
[Cp*(PMe ₃)IrMe(CO)][B(C ₆ H ₃ (CF ₃) ₂) ₄]	$\nu_{\text{CO}} = 2035 \text{ cm}^{-1}$ (KBr)	27b, 64

Cp, Tp, TpMe₂) by Tilset and Skagestad demonstrated that the trispyrazolylborate ligand is more electron donating than the cyclopentadienyl ligand (TpMe₂ > Tp > Cp) toward Cr, Mo, and W (Table 1).^{26,27} While the differences in the ν_{CO} infrared data are relatively small, the electrochemical oxidation of these anions provided strong evidence for the above trend. Unfortunately, this detailed study has been extrapolated incorrectly to other

transition metals.^{28–30} Infrared data for Tp and CpMo alkylidyne complexes reported by McElwee-White and co-workers indicate that the two ligands have relatively similar donor capabilities.³¹ Additional work on group 6 by Sundermeyer and co-workers showed that the Cp* ligand was *more* electron donating than the TpMe₂ ligand for molybdenum and tungsten by comparing the $\nu_{\text{M=O}}$ stretches for a series of LM(O)₂ (L = Cp*, TpMe₂; M = Mo, W) complexes.³²

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(27) (a) Reversible potential. (b) Data acquired for this report. Data obtained from commercially available materials unless otherwise noted.

(28) While unsubstantiated, it has been noted that Tp is more donating toward both titanium and zirconium (see ref 29) and ruthenium (see ref 30).

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For manganese, the infrared data are somewhat ambiguous, but the following trend can be surmised: $\text{Cp}^* \approx \text{Tp}^{\text{Me}_2} > \text{Cp} \approx \text{Tp}$ (Table 1).^{33–35} A more definitive trend is obtained from the available infrared data for technetium: $\text{Cp}^* > \text{Tp}^{\text{Me}_2} > \text{Tp}$ (Table 1).^{36,37} For rhenium, infrared and X-ray crystallographic data for a variety of carbonyl and oxo species yield the following order: $\text{Cp}^* > \text{Tp}^{\text{Me}_2} > \text{Tp} > \text{Cp}$.^{35,36,38–43}

Groups 8 and 9. Data for the group 8 and 9 metals, with the exception of iron, demonstrated that the Tp ligand is less electron releasing than the Cp ligands. For iron, electrochemical studies showed that the Tp ligand is more donating than the Cp ligand.⁴⁴ The remaining group 8 and 9 metals exhibited the following trend: $\text{Cp}^* > \text{Cp} \approx \text{Tp}^{\text{Me}_2} > \text{Tp}$ (Table 1).^{13,45–64}

Conclusion and Summary

This report has summarized data useful in comparing the electron density at Tp- and Cp-bearing metal centers. A consistent trend across the periodic table in the relative electron-donating abilities of these two important ligand classes is clearly lacking. Instead, the

electron donor ability varies with the identity of the metal, its oxidation state, and the other ligands of the complex.⁶⁵ These differences are undoubtedly the result of differences in the bonding nature of Tp and Cp: Tp is a weak-field ligand possessing relatively hard nitrogen σ donors, while the Cp ligand is relatively soft and capable of π donation.² The Tp ligand also strictly enforces an octahedral geometry about the metal center, in contrast to the Cp ligand.^{66–69} These concepts normally provide a foundation for understanding metal–ligand interactions; nonetheless, there is currently no simple explanation for variations in the data summarized in this report. Further understanding will require the synthesis of additional TpM and CpM compounds and new insights about their electronic structures.

This variation in donor ability has importance in the development of non-Cp-based ligands.⁷⁰ In particular, new early and late metal olefin polymerization catalysts have relied heavily on nitrogen-based ligands.⁷¹ As demonstrated in the case of the Tp ligand, switching to these nitrogen-based groups should significantly alter the electronic properties of the metal center. However, it is likely that the electron-donating abilities of these ligands, with respect to Cp, will vary with the identity

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(64) **[Cp*(PMe₃)IrMe(CO)](BARf)**. ¹H NMR (500 MHz, CD₂Cl₂, 25 °C): δ 7.74 (BARf), 7.60 (BARf), 1.97 (d, ⁴J_{P-H} = 2 Hz, C₅Me₅), 1.66 (d, ²J_{P-H} = 11 Hz, PMe₃), 0.56 (d, ³J_{P-H} = 6 Hz, Ir-Me). ¹³C{¹H} (125 MHz, CH₂Cl₂, 25 °C): δ 167.4 (d, ²J_{P-C} = 11 Hz, Ir-CO), 161.9 (d, ¹J_{B-C} = 50 Hz, i-BARf), 135.0 (s, o-BARf), 129.1 (qq, ²J_{F-C} = 31 Hz, ⁴J_{F-C} = 3 Hz, m-BARf), 124.8 (q, ¹J_{F-C} = 270 Hz, BARfCF₃), 117.7 (septet, ³J_{F-C} = 4 Hz, p-BARf), 102.5 (d, ²J_{P-C} = 1 Hz, C₅Me₅), 15.6 (d, ¹J_{P-C} = 41 Hz, PMe₃), 9.32 (s, C₅Me₅), -24.8 (d, ²J_{P-C} = 6 Hz, Ir-Me). ¹⁹F (376.5 MHz, CD₂Cl₂, 25 °C): δ -60.9. ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂, 25 °C): δ -38.4. IR (KBr): 3000 (w), 2920 (w), 2034 (s, CO), 1611 (w), 1356 (s), 1279 (s), 1132 (vs), 954 (m), 899 (m), 839 (w), 714 (m), 683 (m). Anal. Calcd for C₄₇H₃₉IrPOBF₂₄: C, 43.10; H, 3.00. Found: C, 43.02; H, 3.22.

(65) Giering and co-workers have catalogued a series of ligands using a common set of stereoelectronic parameters. They have demonstrated that the parameters assigned to a given ligand are dependent on the nature of the coordinated transition metal. Therefore, variations in the overall electron donor abilities of the ligands across the transition metal series are possible. See: Fernandez, A.; Clementina, R.; Prock, A.; Giering, W. P. *Organometallics* **1998**, 17, 2503–2509, and Fernandez, A. L.; Prock, A.; Giering, W. P. *Organometallics* **1994**, 13, 2767–2772.

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of the transition metal.⁷² Data obtained from the Tp ligand may ultimately be useful in the development and understanding of these new nitrogen-based ligands.

In summary, the electronic properties of the Tp ligand should be taken into consideration when it is utilized in place of the Cp ligand, but it is clear from the data provided in this report that generalizations about the relative donating abilities of the two ligands should be discouraged.

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