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A Measure for σ-Donor and π-Acceptor Properties of Diiminepyridine-Type Ligands

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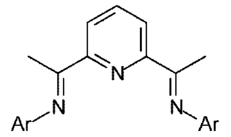
Relative metal−ligand binding strengths for the ZnCl$_2$ and low-spin Co^{I}Me fragments and a variety of diiminepyridine (DIP)-like ligands have been calculated at the DFT level. The assumption of a linear energy relation $\Delta E_{\text{stab}}(\text{F,L}) = \alpha_{\text{F}}\sigma_{\text{L}} + \beta_{\text{F}}\pi_{\text{L}}$ for the relative binding energy of fragment F to ligand L was used to derive scales for ligand parameters σ_{L} and π_{L} representing the σ-donor and π-acceptor qualities of these ligands. The results show that DIP ligands in general are only fair σ-donors but exceptionally good π-acceptors, being eclipsed only by their bis(diazo)pyridine analogues and bis(carbene)pyridine variations. Bis(phosphinimine)pyridines are much poorer π-acceptors than DIP, but are comparable in σ-donor capacity. Introduction of substituents at the pyridine or N-aryl rings of DIP results in changes that are much smaller than the above-mentioned replacement of the ligand side arms. The analysis method also puts metal fragments on a scale for Lewis acidity (α_{F}) and π-basicity (β_{F}). For the series of fragments ScCl$_2$−CuCl$_2$ (all high-spin), results indicate that Lewis acidity increases almost monotonously; π-basicity decreases from ScCl$_2$ to MnCl$_2$ (where it vanishes), is significant again for FeCl$_2$, but negligible for CoCl$_2$−CuCl$_2$.

Introduction

Diiminepyridine (DIP) ligands (Scheme 1) are unique in leading to olefin polymerization catalysts with a wide range of transition metals, including even iron, for which no other olefin insertion polymerization catalysts exist.[1,2] The same ligands are also remarkable in stabilizing metals in a wide variety of oxidation states, which is related to their capacity to act as both σ-donors and π-acceptors. The π-acceptor capabilities of these ligands, in particular, are remarkable: complexes containing metals in *formal* oxidations states down to −2 have been characterized,[3] which places the DIP ligand on a par with carbon monoxide. However, the *nature* of the π-acceptor interaction is strikingly different for CO and DIP: for CO back-donation results from delocalization of a metal-centered electron *pair* to the ligand(s), whereas for DIP-type ligands single-electron transfer prevails, resulting in complexes with ligand-centered unpaired electrons and low singlet−triplet gaps.[4] The relationships, if any, between catalytic activity, easy spin state crossing, and ligand π-acceptor character are not clear at present.

To date, it has been difficult to come up with ligands having comparable properties, and this may in part be due to the fact that it is hard to *quantify* σ-donating and π-accepting capabilities. For phosphines, quantitative analysis of ligand properties started in the 1970s with the Tolman "electronic parameter" χ.[5,6] Computed electronic parameters have been found to work as well as experimental ones,[6c] and this opened the way to prediction of performance for ligands that have not yet been synthesized. Since the work of Tolman, increasingly sophisticated models have been developed to quantify σ-donating and π-accepting properties of ligands, most notably QALE.[7,8] Applying the QALE-type approach to complexes of DIP and related ligands, however, is nontrivial for several reasons. Not enough experimental reference data are available here to allow the sophisticated statistical treatments performed for phosphines. In principle one could, for example, use calculated protonation energies (instead of observed ones[6c]), but the presence of different donor atoms within one ligand makes this procedure somewhat ambiguous.[9] Also, DIP-type ligands are rigid when bound to a metal but flexible when not, and protonation might lead to conformations not relevant to coordination chemistry.

Scheme 1. DIP Ligand



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(1) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

(2) Reviews: (a) Gibson, V. C.; Redshaw Carl Solan, G. A. *Chem. Rev* **2007**, *107*, 1745. (b) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans* **2006**, 5442.

(3) Scott, J.; Vidyaratne, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.*

(4) (a) Knijnenburg, Q.; Hetterscheid, D. G. H.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204. (b) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

(5) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(6) (a) Other "ligand electronic parameters" have been used; see for example: Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271. (b) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980. (c) Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806.

(7) See for example: (a) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, M. M.; Liu, H. Y.; Prock, A; Giering, W. P. *Organometallics* **1987**, *6*, 650. (c) Wilson, M. R.; Prock, A; Giering, W. P.; Fernandez, A. L.; Haar, C. M.; Nolan, S. P.; Foxman, B. M. *Organometallics* **2002**, *21*, 2758.

(8) Kühl, O. *Coord. Chem. Rev.* **2005**, *249*, 693.

(9) Calculating the stretch frequency of, for example, LRh(CO)$^{+}$ would work, similar to the approach used in ref 6c. Unfortunately, that would give us only one single "net electronic parameter" rather than separate values for σ and π components.

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An alternative approach would be to use some kind of energy decomposition scheme to separate metal−ligand interaction energies into σ-and π-components. Such studies have been extremely valuable for understanding metal−ligand bonding in, for example, phosphine and CO complexes,[10] but have not been used much to assign numbers to ligand properties. Unfortunately, many of the ligands we want to study lead to complexes without useful symmetry and often with no clean separation between orbitals involved in donation and back-donation. Given also that different energy decomposition schemes produce very different absolute values for the components of the metal−ligand interaction,[10] we decided not to go this route but stay closer to the ideas behind QALE and the linear free energy relationships often used in organic chemistry.[11] We define the stabilization energy of a metal fragment F by a ligand L (relative to reference ligand L′) via the hypothetical reaction

$$L + L'F \rightarrow LF + L' \quad \Delta E_{\mathrm{stab}}(F,L) \tag{1}$$

Then, we assume that this stabilization energy can be written as a linear energy expression:

$$\Delta E_{\mathrm{stab}}(F,L) = \alpha_F\sigma_L + \beta_F\pi_L \tag{2}$$

where α_F and β_F are measures of the Lewis acidity and π-basicity of the metal fragment, and σ_L and π_L represent the σ-donation and π-acceptor qualities of the ligand (note that a *negative* $\Delta E_{\mathrm{stab}}(F,L)$ means L forms a *more stable* complex with F than the reference ligand L′). Calculation of stabilization energies for two different reference metal fragments, together with an appropriate choice of α_F/β_F for these reference fragments, would then suffice to determine the σ_L/π_L parameters for any ligand. In the present paper, we try to evaluate the usefulness of this approach by addressing the following issues:

- Can one really represent stabilization energies by such a two-term linear energy expression?
- Can one choose the reference fragments and their α_F/β_F values such that the resulting σ_L/π_L parameters are indeed meaningful measures of ligand σ-donation and π-acceptor qualities?
- Assuming this approach is valid, how do various modifications of the original DIP ligand (substituents at pyridine ring or N-aryl groups;[12] replacing the pyridine nucleus by pyrazine or triazine;[13] changing the imine arms to phosphinimines,[14] carbenes,[15] or amines[16]) compare in a quantitative sense?

Unlike in the standard QALE approach,[7note,b] we do not yet attempt to include separate terms representing steric factors. Thus, the resulting σ_L/π_L parameters represent *net* ligand properties *including* any contribution from sterics. For that reason, we do not expect them to be transferable between metal fragments F of very different steric requirements, and we restrict ourselves to fragments that are small and differ mainly in their electronic properties. As reference fragments, we chose $ZnCl_2$ (for which back-donation should be negligible) and low-spin CoMe (for which in DIP complexes transfer of a full electron to the ligand occurs, indicating massive back-donation[4a]).

Methods

All geometry optimizations were performed at the restricted (free ligands, $MgCl_2$ and $ZnCl_2$ complexes) or unrestricted (all other metal complexes) b3-lyp[17]/SV(P)[18] level using the Turbomole package[19] coupled to the standalone Baker optimizer.[20] Improved single-point energies were then calculated at the SV(P) geometries using the TZVP basis set.[21] Complex stabilization energies reported in the text are pure electronic energies, including neither zero-point energy corrections nor any thermal corrections, since we are primarily concerned with electronic effects; they are also not corrected for BSSE.[22,23] Total energies, $\hat{S}^2$ values and geometries (*xyz* format) for all structures considered are provided in the Supporting Information.

Results and Discussion

Structures of Ligands and Complexes. Scheme 2 shows the ligands studied in this work; ligand **1** was chosen as our reference ligand (L′ in eq 1). CoMe complexes of DIP-type ligands typically have the square-planar coordination geometry expected for a four-coordinate d^8 complex (Figure 1A). They are best seen as singlet biradicals, containing low-spin Co^{II} antiferromagnetically coupled to a ligand radical anion.[4a] Unrestricted DFT calculations in fact produce a broken-symmetry solution, which is a mixture of singlet and triplet states, with $\hat{S}^2$ values in the range of 0.8 to 1.2 (expected: 1.0 for a "pure" 1:1 mixture of singlet and triplet). There are ways to obtain a better approximation to "pure singlet" energies, but these do not always work,[24] so we decided to use the unmodified unrestricted DFT energies in the present work.

$ZnCl_2$ complexes typically have a strongly distorted square-pyramidal (SPy) geometry, with two inequivalent chlorine atoms (Figure 1B). Most other metal dichloride fragments optimized

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[10] See for example: Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. M. *Organometallics* **2007**, *26*, 2637, and references therein.

[11] See for example: (a) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; p363−375, and references therein. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

[12] Kleigrewe, N.; Steffen, W; Blömker, T; Kehr, G; Fröhlich, R.; Wibbeling, B.; Erker, G.; Wasilke, J.-C.; Wu, G.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13955.

[13] Britovsek, G. J. P.; Gibson, V. C.; Hoarau, O. D.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2003**, *42*, 3454.

[14] (a) Kreischer, K.; Kipke, J.; Bauerfeind, M.; Sundermeyer, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1023. (b) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Br; ès, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247.

[15] (a) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S. *Organometallics* **2004**, *23*, 4807. (b) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. *Organometallics* **2004**, *23*, 6288.

[16] Britovsek, G. J. P.; Gibson, V. C.; Mastroianni, S.; Oakes, D. C. H.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 431.

[17] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Note that the Turbomole functional "b3-lyp" is not identical to the Gaussian "B3LYP" functional.

[18] Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

[19] (a) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. (b) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346. (c) Ahlrichs, R.; et al. *Turbomole* Version 5; Theoretical Chemistry Group, University of Karlsruhe, January 2002.

[20] (a) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385. (b) *PQS* Version 2.4; Parallel Quantum Solutions: Fayetteville, AR, 2001; the Baker optimizer is available separately from PQS upon request.

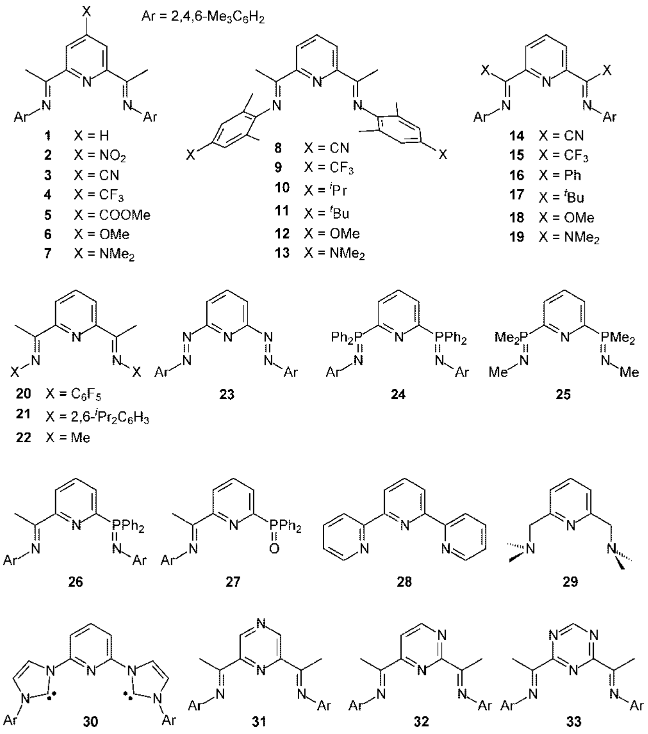
[21] Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

[22] (a) Jansen, H. B.; Ross, P. *Chem. Phys. Lett.* **1969**, *3*, 140. (b) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

[23] A counterpoise correction would be somewhat problematic in any case because the free and complexed CoMe reference fragments have very different orbital occupation patterns. A similar problem applies to the FeMe, $Fe(N_2)$, and $ScCl_2-CuCl_2$ fragments mentioned later in this work.

[24] Given the energy and $\hat{S}^2$ value of the broken-symmetry solution and the energy of the "pure triplet" calculated at the same geometry, one can estimate the "pure singlet" energy.[25] Unfortunately, for many of the structures studied here triplet calculations converge to the "wrong" triplet (one in which d_{z^2} is half empty; the singlet usually has d_{xz} half empty). Because of lack of symmetry, the correct occupation can often not be forced. Since we need a measure that can be calculated straightforwardly for a wide variety of ligands, we decided to standardize on uncorrected UDFT values.

Scheme 2. Ligands Studied in This Work



to similar structures, although in a few cases structures closer to C_{2v} trigonal bipyramidal (TBP) were found to be preferred (Figure 1C). All d^1-d^9 MCl$_2$ complexes were found to prefer high-spin states with little spin contamination. Where literature structures are available for comparison, calculated metal–ligand bond lengths are systematically too long by ca. 0.05 Å.[4a] Apart from this difference, and the amount of distortion along the soft TBP–SPy interconversion coordinate for some dichloride complexes, agreement of observed and calculated structures is good (for a list of relevant observed structures, see Table S17 in the Supporting Information).

Unlike their coordination complexes, free DIP-type ligands are rather flexible. According to limited explorations of conformational space, the lowest-energy conformation tends to be an extended geometry with NCCN torsion angles close to 180° (Figure 1D); this is also the conformation found in most X-ray structure determinations of free ligands (see the Supporting Information). To form a complex, the imine arms must rotate to produce a "closed" structure with NCCN dihedral angles close to 0° (Figure 1E), which in most cases appears to be a local minimum (for ligand **28**, a closed structure was approximated by constraining the two NCCN angles to 0°). Formation of the closed from the extended geometry costs a significant amount of reorganization energy,[26] but this cost is not related to the σ-donation or π-back-donation capabilities of the ligand. Therefore, we apply eq 2 to *closed* conformations of all ligands and provide differential reorganization energies ($\Delta E_{\mathrm{reorg}}$(L), relative to reference ligand **1**) separately in Table 1. The net binding energy of fragment F to ligand L (relative to ligand **1**), with all ligands in their lowest-energy conformations, is then

$$\Delta E_{\mathrm{bind}}(\mathrm{F,L}) = \Delta E_{\mathrm{reorg}}(\mathrm{L}) + \alpha_{\mathrm{F}}\sigma_{\mathrm{L}} + \beta_{\mathrm{F}}\pi_{\mathrm{L}} \qquad (3)$$

Whereas absolute reorganization energies are substantial (e.g., 13.2 kcal/mol for **1**), the differential reorganization energies $\Delta E_{\mathrm{reorg}}$ are much smaller for the pure DIP-type ligands (**2**–**13**, **20**, **21**: up to ±1 kcal/mol). The cost of reorganization seems to be mainly due to unfavorable relative orientations of imine and pyridine group dipole moments in the closed conformation. Significantly less unfavorable reorganization energies are found for ligands **23**, **29**, **32**, and **33**. For the former two ligands, this is due to differences in the groups involved (azo or amine vs imine). For the latter two, addition of ring nitrogen atoms means that for one (in **32**) or two (in **33**) imine arms 180° rotation no longer makes a difference to the local environment and hence does not cost much energy.

The imine arms could potentially also undergo *cis*–*trans* isomerization of the C=N moiety. For ligands bearing bulky groups at the imine carbon (**16**, **17**), the isomerized forms are probably lower in energy than the original ligands. These isomers are, however, not directly relevant to the coordination chemistry we are studying and hence have not been considered in the present work. A consistent way of including this possibility would be to treat *cis*–*trans* isomerization as part of the reorganization energy.

Fragment Stabilization Energies. Table 1 contains the relevant ZnCl$_2$ and CoMe fragment stabilization energies. Systematic variation of parts of the ligand structure was used to analyze trends in fragment stabilization energies. Figure 2 shows the effect of various substituents at the 4-position of the pyridine ring (ligands **2**–**7**) plotted against Taft σ_p and σ_p^- parameters.[27] Electron-withdrawing groups ($\sigma_p^- > 0$) stabilize the CoMe fragment, while electron-donating groups have the opposite effect, demonstrating that π-back-donation provides the dominant contribution to the metal–ligand bonding energy component in this Co$^{\mathrm{I}}$ series. For ZnCl$_2$, on the other hand, withdrawing groups result in a destabilization, indicating that donation is more important.

Interestingly, substitution by electron-withdrawing groups at the 4-position of the N-aryl rings (ligands **8**–**13**) results in a destabilization of *both* ZnCl$_2$ and CoMe fragments. For ZnCl$_2$, this is the expected behavior. For CoMe, it seems that back-donation, although it is the dominant interaction, is not much affected by the substitution, so that the *effect* of the substituents on the σ-donating interaction still prevails. One reason could be that the π-systems of the N-aryl groups are nearly orthogonal to that of the ligand skeleton (pyridine ring + imine arms), as illustrated in Figure 1(A–C). In addition, the coefficients of the ligand π^* orbitals at the imine nitrogens are relatively small. Whatever the reason, the final result appears to be that, even for CoMe, substituents at the 4-position of the N-aryl ring mainly affect σ-donation to the metal center.

We have also looked at variations at the imine carbon atom (ligands **14**–**19**). Substituent effects are quite large, since

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(25) (a) Noodleman, L.; Norman, J. G. *J. Chem. Phys.* **1979**, *70*, 4903. (b) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737. (c) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316. (d) Bachler, V.; Chaudhuri, P.; Wieghardt, K. *Chem.–Eur. J.* **2001**, *7*, 404. (e) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179. (f) Onishi, T.; Takano, Y.; Kitagawa, Y.; Kawakami, T.; Yoshioka, Y.; Yamaguchi, K. *Polyhedron* **2001**, *20*, 1177.

(26) Rotation of the imine arms from the extended to the closed conformation is not the only reorganization needed for complex formation. In addition, formation of the tridentate chelate structure requires changes in several skeleton bond angles. However, the details of these deformations differ from complex to complex and so cannot easily be represented by a single "reorganization energy" value. Therefore, we chose to include in our $\Delta E_{\mathrm{reorg}}$ *only* the energy associated with the extended→closed conformational change.

(27) The σ_p parameter measures the influence of *para* substituents on the rate of hydrolysis of benzoic acids: $\sigma_p(X) = \log\{k_X/k_H\}$. The related σ_p^- parameter was developed for special cases where an electron-withdrawing group interacts with a developing negative charge, which seems to be a fair description of electron transfer from the metal to the ligand π^* orbitals. See ref 11 for details.

(28) ρ is the linear correlation coefficient between the two sets of data.

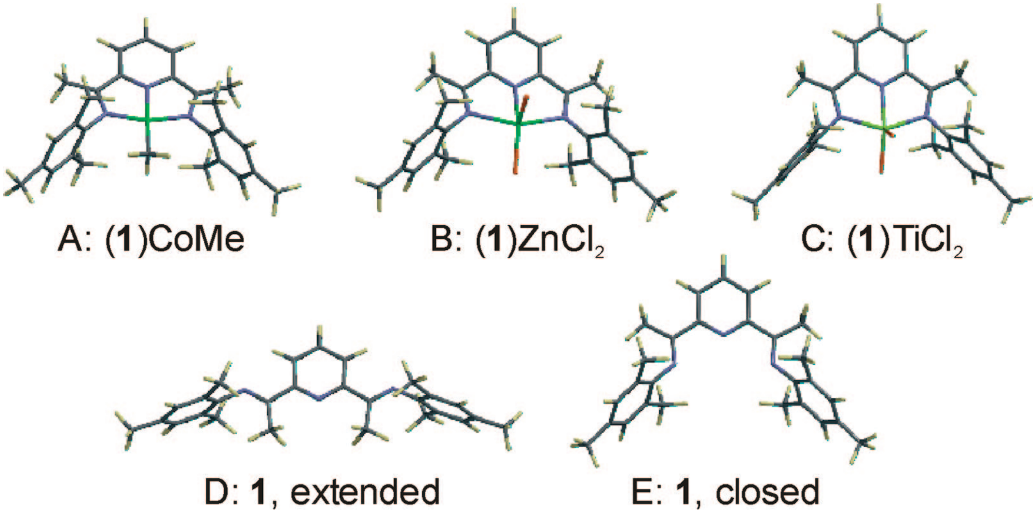

Figure 1. Calculated structures of reference ligand **1** and some of its complexes.

Table 1. Fragment Stabilization Energies, σ_L/π_L Parameters, and Ligand Reorganization Energies (kcal/mol)

ligand	$\Delta E_{stab}(ZnCl_2)$, σ_L	ΔE_{stab}(CoMe)	π_L	ΔE_{reorg}
1	(0)	(0)	(0)	(0)
2	3.46	−7.33	−8.19	−0.84
3	3.05	−4.17	−4.93	−0.23
4	2.40	−2.27	−2.87	−0.28
5	1.02	−3.76	−4.01	−0.96
6	−1.26	2.73	3.05	0.46
7	−3.49	4.09	4.96	0.91
8	3.50	2.76	1.88	−1.12
9	2.77	2.15	1.45	−0.77
10	0.09	0.23	0.21	−0.06
11	1.09	0.10	−0.17	−0.02
12	−0.40	−0.42	−0.32	−0.31
13	−1.55	−1.26	−0.87	0.26
14	9.92	−5.37	−7.85	−7.43
15	10.67	1.60	−1.07	−7.03
16	2.13	−0.09	−0.63	−5.30
17	6.76	6.09	4.40	−1.94
18	3.45	13.78	12.91	−9.95
19	7.95	15.08	13.09	−4.80
20	8.46	−0.09	−2.21	0.49
21	1.41	0.96	0.61	−0.26
22	−10.16	−6.84	−4.30	1.79
23	11.39	−2.36	−5.21	−11.33
24	4.31	18.80	17.73	−3.70
25	−15.16	2.16	5.95	−0.08
26	1.93	7.28	6.80	−2.41
27	3.10	8.45	7.67	0.67
28	−6.01	−1.65	−0.15	2.36
29	−6.48	26.43	28.05	−6.09
30	−17.54	−17.42	−13.03	5.40
31	3.06	−1.10	−1.87	−1.51
32	2.50	0.47	−0.15	−5.80
33	5.50	2.80	1.42	−12.23

substitution occurs at an atom close to the metal center that also bears a large coefficient in the ligand π^* orbitals. These variations are a complex mixture of electronic and steric effects,[29] so there is no clear correlation with, for example, σ_p parameters.

Linear Energy Relation: Separating σ- and π-Effects. Assuming the validity of linear energy relation (2), we need to do the following to define the σ_L/π_L scale:

1. Select a reference ligand to define the zero point of the scale. We have chosen **1** here.

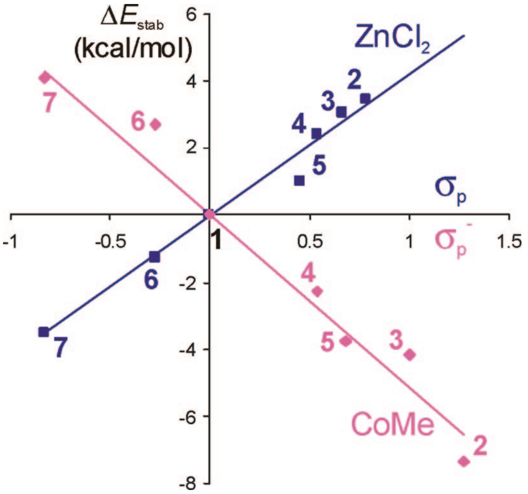

Figure 2. Effect of pyridine 4-substituent on $ZnCl_2$ (blue ■, $\rho^{28} = 0.988$) and CoMe (pink ◆, $\rho = -0.983$) fragment stabilization energies, plotted against Taft σ_p and $\sigma_p{}^-$ parameters.[27]

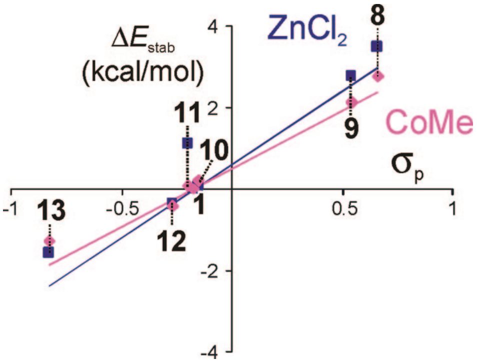

Figure 3. Effect of N-aryl 4-substituent on $ZnCl_2$ (blue ■, $\rho = 0.971$) and CoMe (pink ◆, $\rho = 0.981$) fragment stabilization energies, plotted against Taft σ_p parameters.[27]

2. Choose two reference fragments with rather different Lewis acidity and π-basicity. We have chosen $ZnCl_2$ and low-spin CoMe.

3. Choose α_F and β_F parameters for the reference fragments to give the optimal separation of σ- and π-contributions.

The last part is somewhat problematic. It would be trivial if we could use one reference fragment for which only σ-donation

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[29] For example, the Me_2N group is a strong π-donor (electronic effect), but is forced out of coplanarity with the imine group in the metal complex (steric effect).

was important (i.e., $\beta_F = 0$) and one for which only π-back-donation contributed (i.e., $\alpha_F = 0$). It seems reasonable to assume that back-donation is unimportant for the $ZnCl_2$ fragment. This allows us to set $\alpha_{ZnCl2} = 1$, $\beta_{ZnCl2} = 0$, and so define the σ_L scale. For CoMe, we assume that back-donation dominates, but clearly donation also contributes (see above discussion of substitution at the N-aryl rings). Thus, we can set $\beta_{CoMe} = 1$ but then must assign a nonzero value to α_{CoMe}, presumably $0 < \alpha_{CoMe} < 1$. Unfortunately, there is no clear and objective criterion for choosing this value. We derive a "reasonable" value by requiring orthogonality of variations in σ_L and π_L parameters over our test set of ligands:

$$\sum_{L}(\sigma_L - \overline{\sigma})(\pi_L - \overline{\pi}) = 0$$
$$\overline{\sigma} = \frac{1}{n(L)}\sum_{L}\sigma_L \quad \overline{\pi} = \frac{1}{n(L)}\sum_{L}\pi_L \tag{4}$$

Phrased in a different way, the choice of α_{CoMe} that satisfies equation 4[30] removes any cross-correlation between the σ_L and π_L values, which seems reasonable as long as there is no systematic correlation between σ-donation and π-acceptor properties of the ligands studied. This leads to $\alpha_{CoMe} = 0.25$, which we use in the present work; the consequences of different choices will be discussed below. Having chosen a value for α_{CoMe}, the σ_L and π_L parameters are then obtained from

$$\sigma_L = \Delta E_{stab}(ZnCl_2,L)$$
$$\pi_L = \Delta E_{stab}(CoMe,L) - 0.25\Delta E_{stab}(ZnCl_2,L) \tag{5}$$

The resulting σ_L and π_L values for a wide variety of ligands somewhat related to diiminepyridine are collected in Table 1. Note that these parameters have the dimension of energy and should give an indication of the possible magnitude of ligand effects on, for example, activation energies.

Now that we have a common scale for this diverse set of ligands, it is instructive to compare the effects of various types of ligand variation:

- Substitution at the pyridine ring (ligands **2**−**7**), or replacement of this ring by a pyrazine, pyrimidine, or triazine ring (**31**−**33**), changes both σ_L and π_L by a few kcal/mol.
- Substitution at the N-aryl ring (**8**−**13**, **20**) affects mainly σ_L, and the effect is smaller than for substitution at the pyridine ring.
- Substitution at the imine carbon (**14**−**19**) results in large changes of both σ_L and π_L. The related bis(diazo) ligand **23**[31] is also a better π-acceptor and weaker σ-donor than **1**.
- Replacing the imine arms altogether has the largest effect, ranging from virtually complete loss of π-acceptor character for di*amine*pyridine ligand **29**[16] to a dramatic increase in both σ-donating and π-accepting capabilities for bis(carbene)pyridine ligand **30**.[15] Phosphinimine donor groups (**24**[14]) seem to be comparable to imines in σ-donor strength, but are *much* poorer π-acceptors.

Steric Effects. Unlike energy decomposition schemes like EDA, our analysis does not produce a separate steric term. Rather, the σ_L and π_L parameters are intended to represent the interaction contributions *given* the steric properties of the ligand. In addition, steric effects (in particular due to bulky groups at the imine carbons) affect the reorganization energy, ΔE_{reorg}. In this initial attempt to quantify diiminepyridine ligand properties, we refrain from attempting to parametrize steric effects separately.

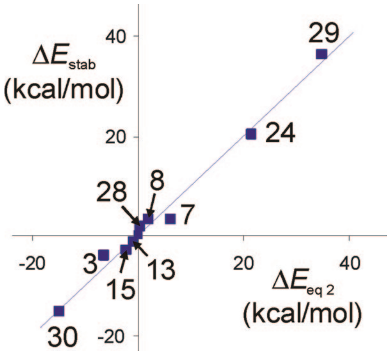

Figure 4. Comparison of calculated $\Delta E_{stab}(FeN_2)$ values with those predicted using the best fit to eq 2 ($\alpha_{FeN2} = -0.07 \pm 0.07$, $\beta_{FeN2} = 1.23 \pm 0.05$; $\rho = 0.994$).

Nevertheless, it is obvious that steric effects are very important. This is illustrated clearly by the difference in σ_L/π_L parameters for N-aryl-bearing reference ligand **1** and N-methyl analogue **22**. There must be some inductive effects here, but the main effect seems to be that reducing the size of the groups at the imine nitrogens allows the metal atom to approach more closely, thus making both σ_L and π_L more negative. The relatively poor σ-donor capabilities of the standard DIP ligand (compare with, for example, di*amine*pyridine **29**), rather than being an intrinsic property of the imine donor group, are therefore caused mainly by the presence of the N-aryl substituents.

Transferability of σ_L and π_L Values. Our ligand-property scale will be useful only if the resulting parameters are also able to describe the stabilization of other metal fragments using eq 2. We tested this by studying a few other small[34] metal fragments in combination with a representative set of test ligands (**1**, **3**, **7**, **8**, **13**, **15**, **24**, **28**−**30**). For each fragment F, α_F and β_F parameters were obtained by fitting to eq 2 using the ligand σ_L and π_L parameters in Table 1; these parameters should represent the Lewis acidity (α_F, relative to $ZnCl_2 = 1$) and π-basicity (β_F, relative to CoMe = 1) of the metal fragment.

The two low-valent fragments FeMe and $Fe(N_2)$ produce fairly good fits, with linear correlation coefficients ρ (between ΔE_{stab} and $\alpha_F\sigma_L + \beta_F\pi_L$) of 0.975 and 0.994, respectively (see Figure 4 for the $Fe(N_2)$ results). The calculated Lewis acidity parameter α_F is zero within error for both fragments, whereas the π-basicity parameter β_F is 0.99 for FeMe and 1.23 for $Fe(N_2)$, indicating that the latter fragment is even more π-basic than CoMe.

Figure 5 summarizes the results obtained in the same manner for the series of MCl_2 fragments, M = Sc−Zn (for individual fits, see the Supporting Information). The quality of the individual fits is generally good, with correlation coefficients of 0.970−0.980 for $TiCl_2$ and $CuCl_2$ and >0.980 for VCl_2−$NiCl_2$; only for the somewhat unusual fragment $ScCl_2$ do we obtain a clearly poorer fit ($\rho = 0.911$) and larger error margins. The data in Figure 5 show that π-basicity (β_F) is largest for $ScCl_2$, then decreases gradually to zero for $MnCl_2$, becomes

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(30) Equation 4 reduces to a linear equation in α_{CoMe} by substituting the definitions $\sigma_L = \Delta E_{stab}(ZnCl_2,L)$, $\pi_L = \Delta E_{stab}(CoMe,L) - \alpha_{CoMe}\Delta E_{stab}(ZnCl_2,L)$ in it.

(31) Ligands of this type have been claimed in a patent,[32] but no synthesis was given there. For synthesis of a mono(diazo) pyridine, see ref 33.

(32) Kerns, M. L.; Bowen, D. E., III; Rodewald, S. German Pat. Appl. DE 100,38,214 A1, 2000.

(33) (a) Campbell, N.; Henderson, A. W.; Taylor, D. *J. Chem. Soc.* **1953**, 1281. (b) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246.

(34) The ligands studied here differ widely in bulk. For larger metal fragments, specific steric interactions will become important and eq 2 is unlikely to hold.

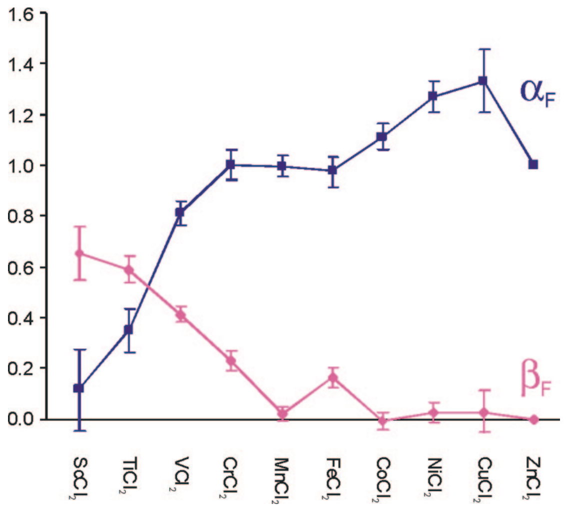

Figure 5. α_F (blue ■) and β_F (pink ◆) values fitted for fragments $ScCl_2$−$ZnCl_2$ and a set of 10 test ligands using eq 2. Error bars indicate 1σ margins.

significant again for $FeCl_2$, but is unimportant for the remaining fragments $CoCl_2$−$CuCl_2$. Lewis acidity (α_F) is lowest for $ScCl_2$ and from there increases nearly monotonously on going to $CuCl_2$.

***π*-Acceptor Character of Bis(carbene)pyridine Ligand 30.** There has been considerable discussion in the literature about the π-acceptor capabilities of Arduengo-type carbene ligands. Originally, these ligands were believed to be very strong σ-donors with negligible π-acceptor character.[35] More recent work indicates that π-back-donation to these ligands is far from negligible, although σ-donation still appears to predominate.[36]

The results we obtain, indicating that ligand **30** is by far the best σ-donor ($\sigma_L = -17.5$) *and* the best π-acceptor ($\pi_L = -13.0$), at a first glance seem to suggest an even greater π-acidity than expected based on literature results. It should be noted, however, that these ligand parameters do *not* reflect the donor/acceptor properties of the carbene groups themselves. In complexes of **30** with low-valent metal fragments, the ligand π-acceptor orbital that becomes populated is concentrated on the pyridine ring and the carbene-fragment *nitrogens*, with only a modest contribution from the carbene carbons. Thus, while our results do not allow us to draw conclusions about the π-acceptor strength of pure carbene ligands in general, they do indicate that bis(carbene)pyridine ligand **30** is exceptionally effective as a σ-donor/π-acceptor ligand. This conclusion is supported in a qualitative sense by the observation that, apart from diimine pyridine ligands themselves, it is the *only* related ligand for which a stable Co^I alkyl has been prepared.[15]

Consequences of Different Choices for α_{CoMe}. The σ_L and π_L parameters for the ligands studied, as well as α_F and β_F values obtained for other metal fragments, depend on the choices of α and β for the two reference fragments $ZnCl_2$ and CoMe. One α and one β parameter can be arbitrarily chosen to define the scale (we chose $\alpha_{ZnCl2} = 1$, $\beta_{CoMe} = 1$). The assumption of negligible back-donation from $ZnCl_2$ seems safe, implying $\beta_{ZnCl2} = 0$. However, our choice of α_{CoMe} is somewhat arbitrary, and it is useful to consider how this choice affects the results.

It should be noted at this point that there is no single "correct" value for α_{CoMe}. The separation between σ- and π-interactions, as implied by eq 2, is only an approximation and cannot be expected to hold exactly for a large number of diverse ligands and metal fragments. We are aiming for a value that works well enough to let us discuss ligand σ-donor and π-acceptor properties in a meaningful manner, while recognizing that there will always be specific effects for particular combinations of fragments and ligands.

The choice of α_{CoMe} affects only the values of π_L, not those of σ_L. Moreover, π_L values would change significantly only for ligands for which $\Delta E_{stab}(ZnCl_2)$ is large relative to ΔE_{stab}(CoMe). To put this in perspective, consider ligand **30**, which for $\alpha_{CoMe} = 0.25$ is predicted to be a strong σ-donor and a strong π-acceptor. On the basis of ideas about weak π-acceptor properties of carbene ligands (as mentioned above), one might prefer a less negative π_L value for this ligand. It is indeed possible to reduce π_{30} to nearly zero (meaning that this ligand would "only" be as strong a π-acceptor as **1**), but this would require setting α_{CoMe} to $\sim$1.0, i.e., assuming its Lewis acidity is as large as that of $ZnCl_2$, which we believe is not very reasonable. Over the range of more reasonable values for α_{CoMe} (which we estimate as 0.15−0.50), the values of π_L for ligands **15**, **17**, **20**, **22**, **29**, and **30** would be significantly affected.

A change in α_{CoMe} also affects parameters fitted for other metal fragments. Values for π-basicity (β_F) remain unchanged, but α_F parameters vary roughly in parallel with α_{CoMe}. This means that the fragments FeMe and Fe(N_2), for which we obtained $\alpha_F \approx 0$, would get a negative Lewis acidity for $\alpha_{CoMe} < 0.25$. While this is not impossible (it would indicate repulsive σ-interactions compensated by stronger attractive π-interactions), it also does not seem very reasonable. Thus, we think that the margins for choosing different α_{CoMe} values (and hence getting significantly different ligand parameters) are limited.

Any choice of α_F/β_F for the reference fragments will produce scales for σ_L/π_L of ligands and for α_F/β_F of other metal fragments. As long as linear dependencies are avoided, any choice will produce the same predicted ΔE_{stab} (eq 2) and ΔE_{bind} (eq 3) values and would lead to the same predictions regarding, for example, catalytic activities. It is only when we want to *interpret* the ligand (σ_L/π_L) and fragment (α_F/β_F) parameters in terms of separate σ- and π-effects that the choice of α_{CoMe} matters, the "best" value leading to the cleanest separation of effects.

Conclusions

We have devised a scale of ligand-property parameters σ_L and π_L for DIP-type ligands that allows a fairly diverse set of ligands to be compared. The parameters are intended to represent overall σ-donating and π-accepting qualities of the ligands, although the approximations implicit in eq 2 and uncertainty about the best choice of α_{CoMe} prevent a clean and unambiguous separation. Nevertheless, the results seem to conform to chemical intuition, showing that the DIP ligand is a very strong π-acceptor, being eclipsed only by bis(carbene)pyridine ligands like **30**. Bis(phosphinimine)pyridine ligands, on the other hand, are reasonable σ-donors but very poor π-acceptors. These results agree with the observation that, up to now, stable Co^I derivatives

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(35) (a) Ho, V. M.; Watson, L. A.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, *27*, 1446. (b) Tafipolsky, M.; Scherer, W.; Ofele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865. (c) Despagnet-Ayoub, E.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 10198. (d) Lee, M. T.; Hu, C. H. *Organometallics* **2004**, *23*, 976. (e) Lai, C. L.; Guo, W. H.; Lee, M. T.; Hu, C. H. *J. Organomet. Chem.* **2005**, *690*, 5867.

(36) (a) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755. (b) Occhipinti, G.; Bjørsvik, H.-R.; Jensen, V. *J. Am. Chem. Soc.* **2006**, *128*, 6952. (c) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350.

have been prepared only for diiminepyridine[37] and bis(carbene)pyridine[15] ligands.

Our definition of ligand parameters naturally leads to scales of metal fragment parameters α_F (reflecting Lewis acidity relative to $ZnCl_2$) and β_F (indicating π-basicity relative to CoMe). Calculations for the series of fragments $ScCl_2-ZnCl_2$ reveal that π-basicity decreases smoothly from $ScCl_2$ (where back-donation dominates over donation) to $MnCl_2$ (negligible back-donation), then is significant again for $FeCl_2$ but unimportant for the later transition metal fragments $CoCl_2-CuCl_2$.

Designing an alternative ligand that matches DIP in both electronic properties and steric shielding is far from trivial. We hope that our scale, or some variation thereof, may be useful in the rational design of such a ligand, or at least in establishing which properties of the ligand are most important for catalytic activity.

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Supporting Information Available: Total energies and $\hat{S}^2$ values for all species mentioned in the text, figures analogous to Figure 4 for the FeMe, $Fe(N_2)$, and MCl_2 (M = Mg, Sc−Cu) fragments, and a zip archive containing all optimized geometries in *xyz* file format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) (a) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719. (b) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252.