Density Functional Study of *N*-Heterocyclic and Diamino Carbene Complexes: Comparison with Phosphines

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In this study we have examined 27 $Cr(CO)_5L$ complexes, ligands including *N*-heterocyclic carbenes (NHCs), acyclic diaminocarbenes, Fischer- and Schrock-type carbenes, and phosphines. We found that NHC−metal bonds are significantly stronger than those of phosphines. Imidazol-2-ylidenes (**1a**−**g**) and their C−C saturated imidazolin-2-ylidene counterparts (**2a**−**g**) demonstrate similar ligand−metal binding and gas-phase proton affinity (PA). CO exchange from $Cr(CO)_6$ by NHCs and carbenes is energetically favorable, while CO exchange for phosphines is unfavorable. NHC ligands facilitate carbonyl dissociation from the complexes to a larger extent than phosphines. It was found that the geometrical parameters and force constants of *trans* C−O in $Cr(CO)_5L$ complexes are closely related to ligand properties such as PA, electronegativity (χ), and charge transfer (ΔN). In general, NHCs and phosphines are nucleophilic and soft ligands, while the nucleophilicity and softness of NHCs are slightly larger. Among them, acyclic diaminocarbenes, imidazolin-2-ylidenes with large substituent groups on nitrogens, and PCy_3 and PPh_3 are ligands that are the softest and most nucleophilic. The nucleophilicity of ligands decrease in the order: $:C(N(i\text{-}Pr)_2)_2 >$ $:C(NMe_2)_2 > PCy_3$, $:C(Me)(NMe_2) > PPh_3$, **2c**−**g** > **1c**−**g**, :C(Me)(OMe), $P(alkyl)_3 > PH_3$, $:C(OH)_2 > :CH_2 > PF_3 > :CF_2$.

1. Introduction

Since the breakthrough of isolating the first *N*-heterocyclic carbenes (NHCs) by Arduengo et al.,[1] preparations of NHC have become accessible to chemists.[2,3] Due to their extraordinary properties, NHC ligands were found to be involved in a great variety of catalytic processes.[4−7] Studies for the applications of NHC ligands in organometallic chemistry have intensified in the past few years. Recent progress in the preparations of NHC complexes has also accelerated the development of NHC-based catalysts in organic synthesis and in various reactions.[6,8] The new generation of NHC catalysts have supplemented the role of traditional phosphine catalysts. Moreover, the phosphine ligands are in part replaced by NHCs due to the demonstrated excellence in homogeneous catalysis of the latter. As stated by Herrmann, a revolutionary turning point in organometallic catalysis is emerging.[6]

The stability of free NHC compounds has received much attention. Theoretical studies were performed to understand the bonding nature of these species. It is known from these studies that the stability of free NHCs is mainly attributed to the $p_\pi - p_\pi$ delocalization of nitrogen atoms. Steric effects also contribute to the stability of NHCs, however to a smaller extent.[9,10] Dimerization is the most likely reaction path for NHCs, and the E_a of dimerization of NHCs with 6π-delocalization (imidazol-2-ylidenes) are ∼10 kcal/mol larger than those of imidazolin-2-ylidenes.[11,12] Steric repulsion is more important for the isolation of imidazolin-2-ylidenes.[13] Contrary to a proposal from experimental study,[14] 4,5-Cl substitutions on NHCs were found to lower the E_a of dimerization.[11,12] A theoretical study from our laboratory shows that the prototype NHC (**1b**, Scheme 1) is not isolable under normal conditions, because it undergoes intermolecular hydrogen transfer readily.[15]

It is generally accepted that NHC binds to metals via σ-bonding, while π-back-bonding of NHC is negligible.[4] A theoretical study by Boehme and Frenking on MCl (M = Cu, Au, Au) complexes reveals that NHC−metal bonds are very strong and that there is negligible π-back-bonding from metal to NHC ligands.[16] The authors have also shown that the aromaticity of NHC ligands is slightly enhanced in the metal complexes and that the ligand−metal bonds have a strong ionic character. Weskamp et al. concluded that the ligand-binding

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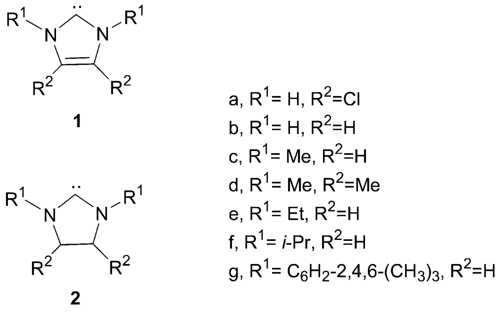
Scheme 1



energies are in the order PH_3 < PMe_3 < **1b** for ruthenium(II)-alkylidene compounds.[17] Similar conclusions was obtained from another theoretical study, in which Schwarz et al. concluded that the ligand binding energies in palladium(II) complexes are in the order PH_3 < PMe_3 < **1b** < **1c**.[18] A spectroscopic study of Öfele et al. reveals the close relationship of NHC and phosphine complexes.[19]

The most successful application of NHCs is probably in second-generation Grubbs' ruthenium−NHC complexes, which catalyze olefin-metathesis reactions.[6,7] A DFT study of Cavallo reveals that phosphine (PCy_3) binding to Ru is stronger with the presence of NHC in the catalyst $(PCy_3)(NHC)Cl_2Ru{=}CHPh$ than in the first-generation catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$. The initiation rate of the NHC-based catalyst is slower, however. The catalytic activity of an NHC-based catalyst is higher due to the higher propensity to olefin coordination and lower activation barriers toward the metathesis products.[20] On the basis of a combined density functional theory (DFT) quantum mechanical/molecular mechanical (QM/MM) study, Adlhart and Chen have also concluded that during a metathesis reaction the second-generation Ru−NHC catalyst has a lower barrier after the olefin coordination step. The higher barrier involved in the reaction of first-generation ruthenium catalysts is attributed to the steric repulsions of phosphine ligands of 3-fold symmetry.[21]

As more and more successful applications of replacing phosphines with NHCs in catalysts are being reported, it is of importance to perform a systematic study on the bonding characters between these two categories of ligands. In previous theoretical studies, only model imidazol-2-ylidenes (**1b** and **1c**) and small phosphines (PH_3 and PMe_3) were investigated. For the purpose of a systematic study, the bonding nature of carbenes is systematically studied using 27 complexes of the type $Cr(CO)_5L$. Several of these complexes were previously studied using theoretical approaches.[17,18,22,23] Knowledge about the difference and similarity between acyclic diaminocarbenes, imidazol-2-ylidenes, imidazolin-2-ylidenes, and phosphines would provide insights into the electronic property and reactivity of these species.

2. Computational Approaches

The theoretical treatment of the systems included in this work was performed by the B3LYP DFT approach using the Gaussian98 series of programs.[24] The B3LYP approach is a hybrid method, which includes Becke's three-parameter nonlocal exchange potential[25] with the nonlocal correlation functional of Lee, Yang, and Parr.[26] We used the 6-31G(d) basis set in the calculations. The 6-31G(d) sets of Cr, Fe, and Ni are Pople's split-valence basis sets with contractions (22s16p4d1f/5s4p2d1f).[27]

Geometries of complexes $Cr(CO)_5L$ were fully optimized. In this study, we included 14 NHCs (**1a**−**2g**, Scheme 1), two diaminocarbenes [$C(NMe_2)_2$ and $C(N(i\text{-}Pr)_2)_2$], six phosphines [PF_3, PH_3, PMe_3, PEt_3, PPh_3, PCy_3], and five other carbene ligands [CH_2, CF_2, $C(OH)_2$, C(Me)(OMe), $C(Me)(NMe_2)$].

Harmonic vibrational frequencies were computed via analytic energy second derivatives at the B3LYP/6-31G(d) level. The frequencies were used to verify whether we have located a genuine minimum and were used to compute zero-point vibrational energy (ZPVE) corrections. ZPVE corrections are included in all energetic calculations. In addition, the force constant (in N cm^{-1}) of the C−O bond *trans* to the ligand $k(C{-}O_{trans})$ was obtained using the energy second derivatives. The σ-donor/π-acceptor ability of a ligand is sometimes measured by the (totally symmetric) carbonyl vibrational frequencies ν(CO) as a result of different M−L bonding. In our study both quantities [$k(C{-}O_{trans})$ and ν(CO)] will be used to characterize ligand−metal bonding.

3. Results and Discussion

Carbene Ligands. The important geometrical parameters of the complexes, $k(C{-}O_{trans})$ and ν(CO), are summarized in Table 1. Definitions of selected geometrical parameters are shown in Scheme 2. In addition, $d(Cr{-}CO_{cis})$ is defined as the average of four $Cr{-}CO_{cis}$ bond distances. τ is defined as the $C_2{-}Cr{-}C_1{-}X$ torsional angle. Among these parameters, R_x represents the proximal N···Cr distance in the substituted five-coordinate complex $[Cr(CO)_4L]$. As mentioned by Tafipolsky et al., the five-coordinate complex is stabilized by the N···Cr bonding.[22] Table 2 shows the ligand exchange energy (ΔE), ligand binding energy (D_0), CO binding energy (D_0'), proton affinity (PA), and singlet−triplet energy separation (ΔE_{S-T}) of carbenes. ΔE is calculated from the following reaction:

$$L + Cr(CO)_6 \rightarrow Cr(CO)_5L + CO$$

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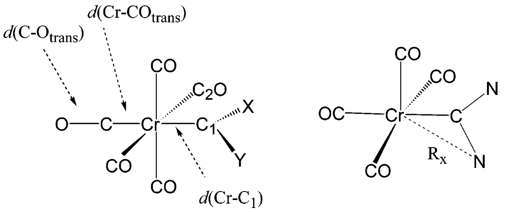
Table 1. Force Constants of *trans* C−O (k(C−O_{trans}), in N cm^{-1}), Vibrational Frequency of the Totally Symmetric CO Stretching Mode (in cm^{-1}), and Important Geometrical Parameters of $Cr(CO)_5L$ Complexes (bond distances in Å, and torsional angles in deg)

	$d(Cr-C_1)$ or d(Cr−P)	$d(Cr-CO_{trans})$	$d(C-O_{trans})$	$d(Cr-CO_{cis})$	R_x	τ	ν(CO)	$k(C-O_{trans})$
1a	2.097	1.882	1.1562	1.900	3.076	0.0	2139.9	17.329
1b	2.107	1.878	1.1573	1.899	3.085	0.0	2136.8	17.210
1c[a]	2.161	1.869	1.1587	1.899	3.107	45.7	2130.9	17.068
1d	2.170	1.868	1.1591	1.899	3.055	45.9	2129.2	17.023
1e	2.177	1.867	1.1591	1.900	3.066	44.0	2129.7	17.025
1f	2.185	1.867	1.1591	1.899	3.055	46.2	2130.2	17.015
1g	2.182	1.862	1.1600	1.900	3.065	0.0	2123.5	16.920
2a	2.067	1.890	1.1549	1.903	3.045	−3.6	2143.8	17.464
2b	2.101	1.880	1.1571	1.898	3.061	−11.8	2137.2	17.230
2c	2.157	1.871	1.1584	1.900	2.955	44.1	2134.0	17.090
2d	2.161	1.870	1.1587	1.899	2.956	49.1	2132.0	17.067
2e	2.173	1.869	1.1587	1.900	2.952	44.0	2132.7	17.065
2f	2.186	1.868	1.1589	1.900	2.936	46.8	2130.6	17.037
2g	2.190	1.863	1.1596	1.900	2.943	0.0	2126.7	16.950
$:C(NMe_2)_2$	2.186	1.871	1.1586	1.900	2.870	27.7	2129.2	17.065
$:C(N(i\text{-}Pr)_2)_2$[a]	2.245	1.866	1.1594	1.899	2.257	19.1	2121.5	16.976
$:C(Me)(NMe_2)$	2.136	1.879	1.1580	1.902	2.900	40.7	2134.5	17.171
$:CF_2$	1.943	1.921	1.1500	1.916		0.0	2171.4	18.017
$:C(OH)_2$	2.021	1.896	1.1545	1.908		44.8	2154.1	17.511
:C(Me)(OMe)	2.020	1.904	1.1544	1.906		−5.2	2145.2	17.495
$:CH_2$	1.914	1.945	1.1496	1.917		−4.3	2166.5	18.016
PF_3	2.250	1.897	1.1505	1.909			2171.7	17.981
PH_3	2.399	1.871	1.1551	1.904			2152.7	17.466
PMe_3	2.416	1.871	1.1564	1.900			2139.6	17.319
PEt_3	2.436	1.869	1.1568	1.898			2135.5	17.262
PPh_3	2.486	1.864	1.1575	1.902			2137.5	17.187
PCy_3[b]	2.578	1.858	1.1584	1.899			2130.8	17.096
CO[c]	1.915	1.915	1.1496	1.915			2190.3	18.072

[a] Geometrical parameters from X-ray data are d(Cr−C1) = 2.138, $d(Cr-CO_{trans})$ = 1.867, $d(C-O_{trans})$ = 1.147, and R_x = 2.207.[19,22] [b] X-ray data: $d(Cr-C_1)$ = 2.422, $d(Cr-CO_{trans})$ = 1.844, $d(C-O_{trans})$ = 1.154, and $d(Cr-CO_{cis})$ = 1.880.[28] [c] X-ray data (averaged): $d(Cr-C_1)$ = 1.915, $d(C-O_{trans})$ = 1.140.[29]

Scheme 2



In general, NHCs and diaminocarbenes have longer $d(Cr-C_1)$ (C_1 is the carbenic carbon), shorter $d(Cr-CO_{trans})$, and longer $d(C-O_{trans})$ than those of other carbenes. 6π-delocalization in NHC does not have a significant effect in the bonding nature of NHC, as $d(Cr-C_1)$ of imidazol-2-ylidene complexes (**1a**−**g**) are very close to their imidazolin-2-ylidene counterparts (**2a**−**g**). The results support that NHC ligands are weak π-acceptors. The π-accepting ability of ligands was assessed with Mulliken population analysis. The changes of overlap populations of p−π atomic orbitals of carbenic carbons during complexation were evaluated. It is seen that the π-accepting ability of NHCs is indeed weaker than those of other carbenes. Among the NHC ligands, **1a**, **1b**, **2a**, and **2b** have shorter $d(Cr-C_1)$ and larger $k(C-O_{trans})$, indicating that their π-accepting abilities are relatively larger. $d(Cr-CO_{cis})$ is rather insensitive to ligands.

NHC rings of **1a** and **1b** complexes are "eclipsed" with the $Cr-CO_{cis}$ bonds; thus the torsional angles (τ) are zero. The rings of **2a** and **2b** are slightly deviated (τ equals 3.6° and 11.8°, respectively) from the eclipsed arrangement. The ring torsional angles of **1c**−**f** and **2c**−**f** are ~45°, resulting from the effect of steric repulsions of substituent groups on the nitrogen atoms.

Table 2. Ligand Exchange Energies (ΔE), Ligand Binding Energy (D_0), CO Binding Energies (D_0') of $Cr(CO)_5L$ Complexes, Proton Affinity (PA), and Singlet−Triplet Energy Separations (ΔE_{S-T}) of Ligands Predicted at the B3LYP/6-31G(d) Approach (in kcal/mol)

	ΔE	D_0	D_0'	PA	ΔE_{S-T}
1a	−10.2	50.0	37.9	247.5	77.6
1b	−13.8	53.7	37.7	258.2	81.6
1c	−8.1	48.0	33.5	266.1	82.9
1d	−7.5	47.4	31.2	272.4	81.7
1e	−4.4	44.3	28.8	269.0	83.7
1f	−7.0	46.9	30.6	271.3	82.7
1g	−6.2	46.0	29.6	275.7	80.0
2a	−10.8	50.7	37.9	242.8	60.8
2b	−14.5	54.4	38.0	260.2	68.5
2c	−6.5	46.3	30.4	266.1	73.5
2d	−7.2	47.0	30.2	270.2	70.0
2e	−6.0	45.9	29.1	268.8	73.4
2f	−5.4	45.3	27.7	270.7	70.8
2g	−4.5	44.4	27.4	274.7	70.7
$:C(NMe_2)_2$	−0.2	40.1	23.8	275.0	40.2
$:C(N(i\text{-}Pr)_2)_2$	−2.5	42.4	21.2	285.9	31.7
$:C(Me)(NMe_2)$	−9.1	49.0	28.2	269.5	31.4
$:CF_2$	−10.1	50.0	38.8	177.2	52.1
$:C(OH)_2$	−6.9	46.7	36.2	234.9	47.8
:C(Me)(OMe)	−17.8	57.7	32.9	253.5	19.7
$:CH_2$[a]	−37.1	76.9	36.2	185.3	−13.1
PF_3	7.7	32.2	41.2	156.1	
PH_3	15.0	24.9	39.6	185.1	
PMe_3	3.0	36.9	39.4	227.2	
PEt_3	2.5	37.3	38.6	233.9	
PPh_3	9.8	30.1	33.2	236.8	
PCy_3	12.4	27.4	26.4	247.2	
CO	0.0	39.9	39.9	103.8	

[a] Energies were computed relative to the singlet state of carbene.

It is, however, somewhat surprising to notice that with the much larger mesityl [C_6H_2-2,4,6-$(CH_3)_3$] group on the nitrogen atoms, **1g** and **2g** adopt eclipsed geometrical arrangements. Magnitudes of $d(\mathrm{Cr-C_1})$ of **1g** and **2g** are unexpectedly short (2.182 and 2.190 Å, respectively); however this does not seem to make the ligand−metal bond stronger (see Table 2). $d(\mathrm{Cr-C_1})$ and $\mathrm{C(N(}i\mathrm{\text{-}Pr)_2)_2}$ are extraordinarily long (2.245 Å) due to its steric repulsion in the complex. Our predicted geometrical parameters of the $\mathrm{Cr(CO)_5L}$ complexes of **1c** and $\mathrm{PCy_3}$ and of $\mathrm{Cr(CO)_6}$ are in close agreement with the X-ray data,[19,22,28,29] while theoretical bond distances are slightly overestimated.

For $\mathrm{Cr(CO)_4L}$ complexes, N···Cr distances (R_x) of acyclic diaminocarbenes are shorter than those of imidazol(in)-2-ylidenes. R_x of $\mathrm{:C(N(}i\mathrm{\text{-}Pr)_2)_2}$ is exceptionally short (2.257 Å), as has been observed experimentally.[22] R_x's of imidazolin-2-ylidenes are shorter than those of imidazol-2-ylidenes, and the D_0' values of the complexes of **2** are also smaller than those of the complexes of **1**.

NHC ligand binding energies range from 44 to 54 kcal/mol, comparable to carbenes such as $\mathrm{:C(OH)_2}$ and $\mathrm{:CF_2}$, and are significantly larger than those of phosphines (25−37 kcal/mol). Consequently, ligand exchange is more favorable for NHCs (negative ΔE) than for phosphines. D_0' values of type **1** carbenes are comparable to their type **2** counterparts. D_0' values of NHCs are larger than those of phosphine complexes. The D_0' values of NHCs are smaller than that of $\mathrm{Cr(CO)_6}$ (39.9 kcal/mol) and are smaller than their corresponding D_0 values. In contrast, D_0' values of phosphine complexes are larger than their corresponding D_0 values. **1a**, **1b**, **2a**, and **2b** are the less stable species among NHCs due to their tendency for dimerization, and we would expect that their $\mathrm{Cr(CO)_5L}$ complexes are more difficult to prepare. However, if these species were made, our computations suggest that their ligand and CO binding would be stronger than those of other NHC ligands. In previous theoretical studies, we have shown that **1a**, **1b** and **2a**, **2b** are less resistant to dimerizations[12] and that **2a** undergoes intermolecular hydrogen transfer to form imidazoles with a very low activation barrier.[15]

The electronic properties of imidazol-2-ylidenes (**1a**−**g**) and imidazolin-2-ylidenes (**2a**−**g**) are quite different. As $\Delta E_{\mathrm{S-T}}$ in Table 2 shows, imdazol-2-ylidenes have much larger singlet−triplet energy separations than their imidazolin-2-ylidene counterparts. This difference is closely related to their stability with respect to dimerization.[12] The difference in electronic property, however, is not directly reflected in the ligand-binding energies. D_0 values of type **1** and **2** complexes are quite similar. The fact that 6π-delocalization does not affect D_0 suggests that π-back-donation may not be important in NHC−metal bonding.

D_0 of the acyclic diaminocarbene $\mathrm{:C(NMe_2)_2}$ is 40.1, several kcal/mol smaller than those of NHC carbenes. In contrast, despite its extraordinarily long $d(\mathrm{Cr-C_1})$, D_0 of $\mathrm{:C(N(}i\mathrm{\text{-}Pr)_2)_2}$ is 2.3 kcal/mol larger than that of $\mathrm{:C(NMe_2)_2}$. $\mathrm{:C(N(}i\mathrm{\text{-}Pr)_2)_2}$ complex has the smallest D_0' among all complexes studied (21.2 kcal/mol), which is attributed to the basicity of the carbene and its ability to stabilize $\mathrm{Cr(CO)_4L}$.

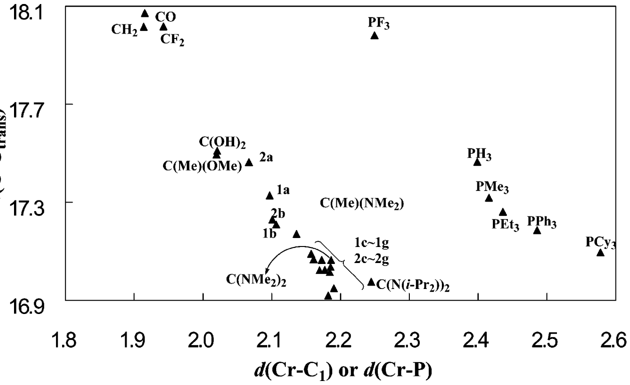


Figure 1. Force constant of *trans* C−O [$k(\mathrm{C-O}_{trans})$, in N cm^{-1}] with respect to bond distances $d(\mathrm{Cr-C_1})$ and $d(\mathrm{Cr-P})$. R^2 of carbenes and phosphines is 0.947 and 0.905, respectively.

The influence of NHC ligands on the electronic properties of complexes can be explored using the IR data of CO groups. The vibrational frequency of C−O stretching is thought to be proportional to the π-back-donating ability of the ligand. Usually, the totally symmetric vibrational mode is used for this purpose. In our study, we have computed the vibrational frequencies and the force constant of *trans* C−O [$k(\mathrm{C-O}_{trans})$]. π-Back-bonding would result in a short Cr−L distance, long $d(\mathrm{Cr-CO}_{trans})$, short $d(\mathrm{C-O}_{trans})$, and large ν(CO) and $k(\mathrm{C-O}_{trans})$. The more basic (σ-donating) ligands will induce smaller vibrational frequencies. We found that the correlation between $k(\mathrm{C-O}_{trans})$ and the C−O totally symmetric frequency [ν(CO)] is fairly good (R^2 = 0.964). Thus for the purpose of extracting electronic properties, both quantities provide proportional information. It will be shown later in our analysis, however, that $k(\mathrm{C-O}_{trans})$ is affected by the change of electron density at the metal (and the carbonyl group) induced by ligands. The difference in $k(\mathrm{C-O}_{trans})$ should not be attributed to π-back-donation alone.

$\mathrm{:CH_2}$ displays a rather short $\mathrm{Cr-C_1}$ and long $\mathrm{Cr-CO}_{trans}$ and $\mathrm{Cr-CO}_{cis}$ bond distances, indicating substantial π-back-donation from the metal. This bonding feature is also revealed by its large ν(CO) and $k(\mathrm{C-O}_{trans})$, as well as by its strong ligand binding (D_0 = 76.9 kcal/mol). In contrast, $\mathrm{:C(Me)(NMe_2)}$ and :C(Me)(OMe) demonstrate relatively longer $\mathrm{Cr-C_1}$ due to their π-basic properties. They also have longer $\mathrm{C-O}_{trans}$ bonds, as well as smaller ν(CO) and $k(\mathrm{C-O}_{trans})$ than those of $\mathrm{Cr(CO)_5(CH_2)}$. $\mathrm{:C(Me)(NMe_2)}$ is more π-basic than :C(Me)(OMe).

Figure 1 plots $k(\mathrm{C-O}_{trans})$ versus $d(\mathrm{Cr-C_1})$ [or $d(\mathrm{Cr-P})$ for phosphine complexes]. In the figure, we see that $k(\mathrm{C-O}_{trans})$ of NHC and diaminocarbene complexes are the smallest among all carbene complexes, again suggesting that NHCs are weak π-acceptors. π-Accepting ability of carbene ligands is in the order Schrock-type > Fischer-type > **2a**−**g** > **1a**−**g**. Within each type of carbenes, steric repulsions reduce π-accepting capacity of the ligands. However, π-accepting capacity is not the only factor that governs ligand−metal bonding: **2a**, **2b**, and **2e** have larger ligand binding energies than their C−C unsaturated counterparts. **2c**, **2d**, **2f**, and **2g**, on the contrary, have smaller ligand binding energies than their C−C unsaturated counterparts. **2g** is the most often used ligand in second-generation ruthenium-based

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metathesis catalysts. D_0 of **2g** is 1.6 kcal/mol smaller than that of **1g**, and D_0' of **2g** is 2.2 kcal/mol smaller than that of **1g**. The strong binding energy of NHC (D_0) to metal is mainly attributed to σ-donation.

With the IR stretching frequencies of carbonyl groups in Rh(carbene)$(CO)_2Cl$ complexes, Denk et al. suggested that acyclic diaminocarbenes are more basic than their cyclic counterparts.[30] Furthermore, C−C saturated NHCs are expected to be stronger σ-donors than their C−C unsaturated counterparts.[6] This point of view was supported by experiments in the reactions of second-generation ruthenium-based metathesis catalysts.[31] From the observations it has been reasoned that type **2** NHCs are more basic than the type **1** NHCs; the higher basicity is then translated into an increased activity of the catalyst.

The computed gas-phase proton affinity (PA) of carbenes (Table 2) shows that the basicity of $:C(N(i\text{-}Pr)_2)_2$ is the strongest among all carbene molecules studied (285.9 kcal/mol). The PA of $:C(NMe_2)_2$ is significantly smaller (275.0 kcal/mol), but is still larger than those of NHCs. This observation agrees with the prediction of Alder et al. that the PA of acyclic diaminocarbene is higher than those of NHCs.[32] The gas-phase basicities of compounds **2**, however, are not necessarily larger than those of their C−C unsaturated counterparts **1**. The use of C−C saturated imidazolin-2-ylidene ligands results in higher catalytic activity in olefin metathesis.[33] However, this is not attributed to the higher PA, as suggested by Denk et al.[30] On the contrary, our computed PA of **1g** is higher than that of **2g**.

The R_x value of **2g** (2.943 Å) is noticeably shorter than that of **1g** (3.065 Å), and the D_0' of **2g** is 2.2 kcal/mol smaller than that of **1g**. The enhanced catalytic activity of **2g** over **1g** in ruthenium-based metathesis reactions could be attributed to the tendency of **2g** to promote phosphine dissociation. From the present analysis, $:C(N(i\text{-}Pr)_2)_2$ has the strongest tendency to weaken a neighboring carbonyl group (by stabilizing the five-coordinated complex). If similar trends are translated into weakening of a phosphine ligand in a complex, $:C(N(i\text{-}Pr)_2)_2$ could enhance the initiation process of the ruthenium-based metathesis.

Phosphine Ligands. Phosphine−metal bonds are much weaker ($D_0 = 25{-}37$ kcal/mol, Table 2) than NHC−metal bonds in $Cr(CO)_5L$ complexes. In contrast to NHC ligands, CO ligand exchange by phosphine ligands is endothermic (ΔE positive). This is in accord with experimental observation that, very often in catalytic processes, excess amounts of phosphines are required in order to sustain the catalytic activity of complexes. For a complex of the largest phosphine ligand (PCy_3), the Cr−P distance is significantly longer (2.578 Å) than those of other phosphine ligands (Table 1). In phosphine complexes, CO binding energies are larger than those of the phosphine ligands (D_0' larger than D_0). The exception is PCy_3, for which D_0 and D_0' are comparable and are smaller than the other phosphines (~27 kcal/mol). Steric repulsion of PCy_3 contributes to the reduced CO binding energy. The steric effect of PCy_3 is also seen in the longest d(Cr−P), shortest $d(\text{Cr}-\text{CO}_{trans})$, and smallest ν(CO) and $k(\text{C}-\text{O}_{trans})$ of its complex. The π-accepting ability of PCy_3 is therefore the smallest among phosphines. The energy required for PCy_3 ligand exchange is relatively large (12.4 kcal/mol). It is seen in Figure 1 that $k(\text{C}-\text{O}_{trans})$ correlates well with d(Cr−P), where $R^2 = 0.905$.

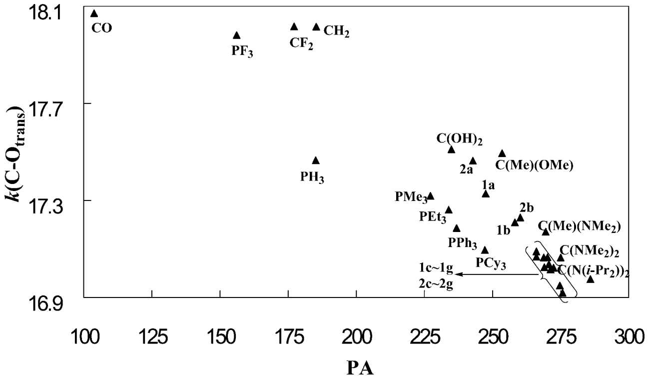

Figure 2. Force constant of *trans* C−O [$k(\text{C}-\text{O}_{trans})$, in N cm^{-1}] with respect to the proton affinity (PA) of ligands. R^2 of carbenes and phosphines is 0.942 and 0.916, respectively. R^2 of all ligands is 0.830.

Phosphines are ordered according to their d(Cr−P) in Tables 1 and 2. The Tolman cone angles for PH_3, PF_3, PMe_3, PEt_3, PPh_3, and PCy_3 are 87°, 104°, 118°, 132°, 145°, and 170°, respectively.[34] d(Cr−P) is approximately proportional to cone angles; that is, large cone angles are associated with long d(Cr−P). The exception is PF_3, due to its extraordinarily strong σ-withdrawing and π-accepting tendency. ν(CO) and $k(\text{C}-\text{O}_{trans})$ are inversely proportional to cone angles, indicating that π-back-bonding of phosphine is hindered by steric repulsions. D_0' decreases as cone angle increases. The phosphine−Cr bond strength in $Cr(CO)_5L$ is not well correlated with the cone angles, however, and the degree of CO substitution from $Cr(CO)_6$ by phosphine is not inversely proportional to the Tolman cone angles (see ΔE in Table 2). Thus, steric effects alone cannot be used as the criteria to assess phosphine−metal bonding.

The PAs of phosphines are summarized in Table 2. It is seen that the gas-phase basicity of phosphines are in general smaller than those of NHCs and diaminocarbenes. The PA of PF_3 is the smallest among all ligands studied. PH_3, $:CF_2$, and $:CH_2$ also have rather small PA values. We have also found that $k(\text{C}-\text{O}_{trans})$ correlates PA of phosphines with $R^2 = 0.916$. For carbenes, R^2 is 0.942 between $k(\text{C}-\text{O}_{trans})$ and PA (see Figure 2). The $k(\text{C}-\text{O}_{trans})$ versus PA relation is plotted in Figure 2. Since the PA is more of the σ effect, the good correlation between PA and $k(\text{C}-\text{O}_{trans})$ [and ν(CO)] suggests that $k(\text{C}-\text{O}_{trans})$ and ν(CO) reveal information about the electron density induced by different ligands on the metal center and the carbonyl groups. They do not necessarily reveal π-back-bonding ability of the ligands, however.

The geometrical and spectroscopic parameters reveal the bonding natures of a complex. Differences in the computed quantities are results of the electronic/steric

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Table 3. Square of Correlation Coefficient (R^2) between the Computed Quantities of Cr(CO)$_5$L Complexes[a]

	d(Cr−C$_1$) or d(Cr−P)	d(C−O$_{trans}$)	ν(CO)	k(C−O$_{trans}$)	PA	χ	ΔN
d(Cr−C$_1$) or d(Cr−P)							
d(C−O$_{trans}$)	0.948 0.910						
ν(CO)	[\] 0.942 [\] 0.848	[\] 0.959 [\] 0.964 [\] 0.954					
k(C−O$_{trans}$)	[\] 0.947 [\] 0.905	[\] 0.998 [\] 1.000 [\] 0.998	0.967 0.966 0.964				
PA	0.875 0.815	0.935 0.911 0.814	[\] 0.947 [\] 0.950 [\] 0.867	[\] 0.942 [\] 0.916 [\] 0.830			
χ	[\] 0.807 [\] 0.826	[\] 0.808 [\] 0.932 [\] 0.829	0.887 0.972 0.905	0.821 0.938 0.843	[\] 0.914 [\] 0.994 [\] 0.799		
ΔN	0.818 0.836	0.780 0.904 0.803	[\] 0.866 [\] 0.945 [\] 0.883	[\] 0.791 [\] 0.909 [\] 0.816	0.877 0.988 0.778	[\] 0.986 [\] 0.992 [\] 0.987	

[a] The first, second, and third entries are R^2 of 21 carbenes, 6 phosphines, and for all 27 ligands, respectively. Quantities that are inversely proportional are labeled with the **[\]** sign.

Table 4. Ligand Exchange Energy (ΔE), Force Constant of *trans* C−O, and Important Geometrical Parameters of Fe(CO)$_4$L and Ni(CO)$_3$L Complexes

	ΔE	k(C−O$_{trans}$)[a]	d(M−C$_1$) or d(M−P)	d(M−CO$_{trans}$)[a]	d(C−O$_{trans}$)[a]
Fe(CO)$_4$L					
1b	−19.6	17.751	1.976	1.793	1.1527
1c	−14.0	17.554	2.010	1.785	1.1543
1e	−12.1	17.487	2.021	1.783	1.1549
1f	−8.6	17.140	2.043	1.774	1.1579
2b	−20.9	17.740	1.973	1.794	1.1528
2c	−11.4	17.553	2.008	1.786	1.1543
2e	−12.7	17.424	2.018	1.783	1.1554
2f	−6.7	17.137	2.043	1.775	1.1579
PMe$_3$	0.5	17.763	2.295	1.781	1.1526
PCy$_3$	4.9	17.559	2.362	1.774	1.1542
CO[b]	0.0	18.370	1.813	1.813	1.1474
Ni(CO)$_3$L					
1b	−14.2	17.531	1.950	1.789	1.1542
1c	−12.3	17.414	1.968	1.787	1.1548
1e	−12.4	17.415	1.983	1.787	1.1550
1f	−8.2	17.406	2.007	1.787	1.1552
2b	−14.9	17.524	1.944	1.789	1.1557
2c	−11.4	17.483	1.980	1.788	1.1545
2e	−11.8	17.434	1.981	1.787	1.1548
2f	−6.8	17.406	2.008	1.787	1.1551
PMe$_3$	2.1	17.698	2.242	1.786	1.1528
PCy$_3$	2.8	17.525	2.304	1.783	1.1540
CO[b]	0.0	18.484	1.811	1.811	1.1462

[a] For Ni(CO)$_3$L, the quantity is taken from the average of three CO ligands; for Fe(CO)$_4$L, the quantity is taken from the *trans* CO ligand. [b] X-ray data for Fe(CO)$_4$L: d(Fe−CO$_{trans}$) = 1.811, d(C−O$_{trans}$) = 1.117; for Ni(CO)$_3$L (averaged): d(Ni−CO$_{trans}$) = 1.817, d(C−O$_{trans}$) = 1.127.[35]

influences of ligands. In Table 3 we summarize the square of correlation coefficients (R^2) between seven computed quantities of Cr(CO)$_5$L and free ligands (inverse proportionality is labeled with the [\] sign). Almost perfect correlation is seen between d(C−O$_{trans}$) and k(C−O$_{trans}$) ($R^2 = 0.998$). However, R^2 between d(C−O$_{trans}$) and ν(CO) is slightly smaller, 0.954 for all 27 complexes. The correlation between the totally C−O stretching ν(CO) and k(C−O$_{trans}$) is fairly high ($R^2 = 0.964$). Ligand−metal distances [d(Cr−C$_1$) or d(Cr−P)] are inversely proportional to ν(CO) and k(C−O$_{trans}$) and are proportional to d(C−O$_{trans}$).

Fe(CO)$_4$L and Ni(CO)$_3$L Complexes. Table 4 shows the ligand exchange energy (ΔE), selected geometrical parameters, and k(C−O$_{trans}$) of Fe(CO)$_4$L and Ni(CO)$_3$L complexes with selected NHC and phosphine ligands. The optimized structures of Fe(CO)$_4$L are close to trigonal bipyramidal (TBP) with axial ligands, while those of Ni(CO)$_3$L are close to tetrahedral. For Fe(CO)$_4$L, attempts to locate the structures of square pyramidal and TBP with L in the equatorial position resulted in the TBP and axial L complex. The predicted geometries of Cr(CO)$_6$, Fe(CO)$_5$, and Ni(CO)$_4$ are in close agreement with X-ray data.[29,35] As expected, the ligand−metal distance is in the order Cr(CO)$_5$L > Fe(CO)$_4$L > Ni(CO)$_3$L. The force constant k(C−O$_{trans}$) is the largest in the Fe complexes, followed by the Ni and Cr complexes, respectively. It is noted, however, that the force constants (and the bond distances summarized in Table 4) of Ni(CO)$_3$L are taken from the average of three CO ligands.

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It is seen that, similar to that of $Cr(CO)_5L$, NHC ligands bind more strongly to metals than phosphines do. Ligand exchange of NHCs with $Fe(CO)_5$ and $Ni(CO)_4$ is exothermic, whereas those for phosphines are endothermic. For NHCs, ΔE values of type **1** and **2** carbenes are comparable. With larger substituents on NHC such as **1f** and **2f**, ligand exchange is less favorable. Comparatively, ligand exchange occurs more readily for **1f** than for **2f**.

Electrophilicity of Carbenes and Phosphines. In the comparative study of different ligands in complexes, the concept of "carbene philicity" is appealing, as it reveals the electronic property of the species. The idea was originated from the definition of the carbene selectivity index m_{CXY} by Moss.[36] Mendez and Garcia-Garibay investigated the electrophilicity and nucleophilicity of a carbene using the charge transfer (ΔN) between carbenes and alkenes.[37]

$$\Delta N = (\chi_C - \chi_D)/2(\eta_C + \eta_D) \qquad (1)$$

Within the finite-difference approximation, χ is the electronegativity defined as (IP + EA)/2,[38] and η is the absolute hardness defined by (IP − EA)/2,[39] where IP and EA are vertical ionization potential and electron affinity, respectively. ΔN is the predicted electron transfer from species D to species C when the reaction between C and D is completed. The more electron transfer from an alkene to the carbene, the more electrophilic the carbene.[37] Sander analyzed carbene philicity using DFT-computed IP and EA. According to his analysis, nucleophilic carbenes are characterized by low IPs and low EAs; electrophilic carbenes, however, have high IPs and high EAs.[40] In Sander's analysis, electrophilicity of a carbene is proportional to the electronegativity χ.

Table 5 summarizes the IP and EA, electronegativity (χ), and molecular hardness (η) of ligands computed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level (in eV). Charge transfer (ΔN) from ligands to $Cr(CO)_5$ was computed using eq 1. χ and ΔN correlate almost linearly ($R^2 = 0.987$). The acyclic diaminocarbene $:C(N(i\text{-}Pr)_2)_2$ has the smallest electronegativity ($\chi = 2.98$) and most negative ΔN (−0.180) among all ligands; it is thus the most nucleophilic ligand. NHCs of types **1** and **2** are also relatively nucleophilic. Type **2** carbenes are slightly more nucleophilic than type **1** carbenes. For phosphines, PCy_3 and PPh_3 are slightly more nucleophilic than most NHCs, and the nucleophilicities of PMe_3 and PEt_3 are comparable to **1c**−**g**. $:CH_2$ is an electrophilic ligand ($\chi = 5.37$), while PF_3, $:CF_2$, and CO are the most electrophilic. Using either the χ or ΔN scale, the nucleophilicity of ligands decreases in the order $:C(N(i\text{-}Pr)_2)_2 > :C(NMe_2)_2 > PCy_3$, $:C(Me)(NMe_2) > PPh_3$, **2c**−**g** > **1c**−**g**, :C(Me)(OMe), $P(alkyl)_3 > PH_3$, $:C(OH)_2 > :CH_2 > PF_3 > :CF_2$.

The electrophilicity/nucleophilicity scale of ligands demonstrates the induced electron density change at the metal center. We thus expect that the DFT-computed quantities χ and ΔN would be correlated with the vibrational frequency or force constant of the carbonyl group in the $Cr(CO)_5L$ complex. The correlations between χ, ΔN, and the geometrical parameters and spectroscopic data of the complexes and the PA of ligands are indeed fairly good (see Table 3). The correlation among χ and ΔN is very high, indicating that both quantities describe the electrophilicity equally well. The correlations between χ and ΔN and other quantities of phosphine ligands are higher than those of carbene ligands. The $k(C{-}O_{trans})$ versus χ relation is plotted in Figure 3.

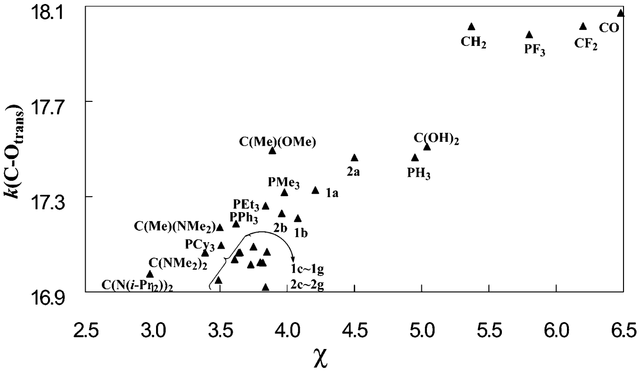

Figure 3. Force constant of *trans* C−O [$k(C{-}O_{trans})$, in N cm^{-1}] with respect to the electronegativity χ of ligands. R^2 of carbenes and phosphines is 0.821 and 0.938, respectively. R^2 of all ligands is 0.843.

Table 5. Ionization Potential and Electron Affinity (IP and EA), Electronegativity (χ), and Absolute Hardness (η) Computed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) Level (in eV)

	IP	EA	χ	η	ΔN^a
1a	8.99	−0.57	4.21	4.78	0.071
1b	8.63	−0.47	4.08	4.55	0.081
1c	8.22	−0.51	3.85	4.37	0.098
1d	8.03	−0.39	3.82	4.21	0.102
1e	8.08	−0.48	3.80	4.28	0.103
1f	7.90	−0.44	3.73	4.17	0.109
1g	8.10	−0.42	3.84	4.26	0.100
2a	9.13	−0.14	4.50	4.64	0.054
2b	8.39	−0.47	3.96	4.43	0.090
2c	7.96	−0.46	3.75	4.21	0.107
2d	7.74	−0.45	3.65	4.10	0.116
2e	7.73	−0.45	3.64	4.09	0.116
2f	7.61	−0.40	3.61	4.01	0.120
2g	7.31	−0.33	3.49	3.82	0.132
$:C(NMe_2)_2$	7.20	−0.43	3.39	3.81	0.139
$:C(N(i\text{-}Pr)_2)_2$	6.32	−0.37	2.98	3.35	0.180
$:C(Me)(NMe_2)$	7.47	−0.47	3.50	3.97	0.128
$:CF_2$	12.38	0.03	6.20	6.17	−0.046
$:C(OH)_2$	10.26	−0.18	5.04	5.22	0.018
:C(Me)(OMe)	8.19	−0.40	3.89	4.30	0.096
$:CH_2{}^a$	10.46	0.28	5.37	5.09	−0.002
PF_3	12.50	−0.90	5.80	6.70	−0.023
PH_3	10.57	−0.66	4.95	5.62	0.022
PMe_3	8.57	−0.61	3.98	4.59	0.087
PEt_3	8.17	−0.49	3.84	4.33	0.099
PPh_3	7.54	−0.30	3.62	3.92	0.121
PCy_3	7.38	−0.36	3.51	3.87	0.129
CO	14.23	−1.28	6.48	7.76	−0.052
$Cr(CO)_5$	8.55	2.14	5.34	3.21	

[a] Charge transfer (ΔN) from ligands to $Cr(CO)_5$ were computed using eq 1.

The computed absolute hardness also reveals the property of ligands. The inverse of η is the softness (S) of a molecule, which was shown by Yang and Parr to be associated with the polarizability of the molecule.[41] $:C(N(i\text{-}Pr)_2)_2$, which has the smallest absolute hardness

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of $\eta = 3.35$, is the "softest" species in Table 4. :C(NMe$_2$)$_2$ and **2g** are also among the softest species studied, followed by PCy$_3$, PPh$_3$, :C(Me)(NMe$_2$), and NHCs. The softness of type **2** NHCs is slightly larger than those of type **1** NHCs. Comparatively, **2g** is softer and more nucleophilic than **1g**. Overall, we find that NHCs and phosphines are soft, polarizable ligands.

4. Conclusion

A systematic study of the complexes Cr(CO)$_5$L has been performed using theoretical DFT approaches, with L being NHCs, diaminocarbenes, Fischer- and Schrock-type carbenes, and phosphines. It has been observed that ligand−metal bonds of NHCs are much stronger than those of phosphines. NHC ligand binding energies are larger than their CO binding energies, while for phosphine complexes the CO binding energies are stronger. CO exchange from Cr(CO)$_6$ by NHCs and carbenes is energetically favorable, while for phosphines CO exchange is unfavorable. Steric repulsion further reduces the π-accepting capacity of a ligand. π-Back-donation is negligible in NHC−metal bonding. In terms of reporting electronic properties of the C−O vibrations, we found that k(C−O$_{trans}$) and from the totally symmetric carbonyl stretching mode ν(CO) are approximately proportional.

It was also found that the gas-phase basicity of C−C unsaturated NHCs is comparable to their C−C saturated counterparts. :C(N(i-Pr)$_2$)$_2$ is most basic among all ligands; however this basicity is not transferred into ligand binding. :C(N(i-Pr)$_2$)$_2$ has an extraordinary ability to stabilize the five-coordinate complex Cr(CO)$_4$L and thus facilitates the extrusion of CO in Cr(CO)$_5$L. In general, the basicity of ligands decreases in the order diaminocarbenes > NHCs > phosphines.

Geometrical parameters and k(C−O$_{trans}$) in Cr(CO)$_5$L correlate well with PA, χ, and ΔN. NHCs and phosphines are nucleophilic, soft ligands. The nucleophilicity and softness of NHCs are slightly larger than those of phosphines. Acyclic diaminocarbenes, imidazolin-2-ylidenes with large substituent groups on nitrogens, and PCy$_3$ and PPh$_3$ are ligands that are the softest and the most nucleophilic. The nucleophilicity of ligands decreases in the order :C(N(i-Pr)$_2$)$_2$ > :C(NMe$_2$)$_2$ > PCy$_3$, :C(Me)(NMe$_2$) > PPh$_3$, **2c**−**g** > **1c**−**g**, :C(Me)(OMe), P(alkyl)$_3$ > PH$_3$, :C(OH)$_2$ > :CH$_2$ > PF$_3$ > :CF$_2$.

The overall activity of a complex is the result of interplay between the electronic and steric effects of the ligand. Our analysis concerning the effect of ligands on the properties of complexes provides insights for the tuning of the ligand environment in catalysts. Knowledge of the structure/property relations from this study would benefit future catalyst designs.

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