N-HETEROCYCLIC CARBENES OF THE LATE TRANSITION METALS:

A COMPUTATIONAL AND STRUCTURAL DATABASE STUDY

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A computational chemistry analysis combined with a crystallographic database study of the bonding in late transition metal N-heterocyclic carbene (NHC) complexes is reported. The results illustrate a metal-carbon bond for these complexes, approximately 4% shorter than that of a M-C single bond found in metal alkyl complexes. As a consequence of this result, two hypotheses are investigated. The first hypothesis explores the possibility of multiple-bond character in the metal-carbon linkage of the NHC complex, and the second, considers the change in the hybridization of the carbenoid carbon to incorporate more p character. The latter hypothesis is supported by the results. Analysis of these complexes using the natural bond orbital method evinces NHC ligands possessing trans influence.

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CHAPTER 1

INTRODUCTION

There has been considerable experimental interest in the chemistry of N-heterocyclic carbenes (NHCs) following upon the work of Arduengo [1]. His work focused on methods leading to the formation of $M(NHC)_2$ complexes (scheme 1).

Scheme 1. Arduengo's starting material (a), imidazolium, for the formation of the bis-carbene metal complex (b).

Much of the industrial and academic interest in NHC complexes has been formulated on the basis of these ligands as phosphine (PR_3) equivalents. NHCs examined in this paper are those derived from imidazoles, pyrazoles, triazoles and Wanzlick dimers (scheme 2) [2].

Scheme 2. NHC ligands derived from (a) imidazoles, (b) pyrazoles, (c) triazoles and (d) Wanzlick dimers; R = H, CH_3 , C_xH_y .

NHCs not only mimic phosphine ligands, but they possess a clear advantage over phosphines due to the TM-NHC complexes' "high thermal and hydrolytic durability" [2] resulting from very stable M=C bonds that are highly resistant to oxidation. The NHC ligands' "easy accessibility" has also been demonstrated [2], thus increasing their popularity as substitutes for the classical $2e^-$ donor ligands such as amines, ethers, and phosphines. Industrially, the use of TM-NHC complexes as catalysts increased mainly because there is "no need for an excess of the ligand" to complete a reaction, thus cutting the costs tremendously [2]. Due to their burgeoning acceptance as $2e^-$ donor ligands, NHCs found use in a wide variety of organometallic reactions. For example, NHC complexes of Pd have been investigated for their utility in the Heck coupling reaction in organic synthesis [3]. The Heck coupling reaction utilizes NHC complexes as catalysts (scheme 3).

Scheme 3. NHC catalysts used in Heck coupling reaction. X = Cl, Br, I.

Complexes 3a and 3b are extremely stable and become active when reduced with formate or hydrazine to generate the Pd^0 species. Augmenting the TM-NHC's incredible preponderance, the low catalyst loadings necessary to obtain yields greater than 99% are

less than 10^{-3} mol% (X=Br) and between 0.1 and 1.0 mol % if X=Cl [4]. Grubbs and coworkers have studied NHC complexes of Ru for ring closing metathesis reactions [4]. Their proposed catalyst 4a although it has a lower reactivity at room temperature than the parent catalyst 4b, but at a little bit higher temperatures its reactivity escalates tremendously.

Scheme 4. Grubbs' proposed catalyst for the olefin metathesis reactions. One of the phosphine groups has been replaced by a NHC ligand with significant increase in reactivity at slightly elevated temperatures.

Herrmann *et al.* studied the chemistry of TM-NHC complexes for industrially important catalytic reactions such as ketone hydrosilation and furan synthesis [2]. In addition to their industrial importance, there is evidence that NHCs may form under physiological conditions as a result of in vivo Maillard reactions [5]. Among other important catalytic reactions involving TM-NHC complexes are: Suzuki-Miyaura (5a), Suzuki Coupling (5b), Aryl Amination (5c), Amide α -Arylation, Sonogashira Coupling and C-H Activation [2].

(a)

(b)

(c)

Scheme 5. Suzuki Miyaura (a) $R = \text{H}, 3,5\text{-(OCH}_3)_2, 4\text{-CO}_2\text{CH}_3$, cat = $\text{Pd(OAc)}_2 + \text{NHC}$; Suzuki Coupling (b) $R = \text{H}, \text{CH}_3, \text{CO}_2\text{CH}_3$, cat = $[\text{Pd}_2(\text{dba})_3] + \text{NHC}$; Aryl Amination (c) $R_1 = \text{H}, 2\text{-CH}_3, 4\text{-CN}, 4\text{-OCH}_3$, $R_2, R_3 = \text{alkyl, aryl, (hetero)cyclic alkyl}$, cat = $[\text{Pd}(\text{dba})_2]$ or $[\text{Pd}_2(\text{dba})_3] + \text{NHC}$

Beyond catalysis, NHCs have gained relevance in the field of materials science.

Liu et al. describes thermally stable liquid crystals based on NHC-palladium complexes (scheme 6) [6]. Given their importance, this paper will augment previous studies on TM-NHC complexes hoping to answer some questions about the nature of their bonding.

Scheme 6. Liu's NHC-palladium complex forming the basis for a novel type of thermally stable liquid crystals.

Stable NHCs have been ligated to a wide variety of transition metals (TMs) and in many respects their complexes comprise a third family of carbene complexes in addition to the Fischer and Schrock-type archetypes [7] construed by complexes such as $\text{Cr(CO)}_5(=\text{C(OMe)Ph})$ [8] and $(\text{neopentyl})_3\text{Ta}=\text{C(H)t-Bu}$ [9], respectively. NHC complexes are found in a variety of chemical environments and for a variety of transition metals not seen for prototypical Fischer- and Schrock-type carbenoid ligands. For example, NHC complexes of silver [10] and mercury [11] have been structurally characterized. Additionally, *bis*-NHC complexes such as $\text{NiI}_2(\text{NHC})_2$ [12] and Ni(NHC)_2 [13] are without analogues for Fischer- and Schrock-type ligand sets. It is reasonable, therefore, to probe the nature of the bonding in the metal-carbon linkage of NHC complexes, particularly those involving later transition metals (i.e., those of Groups 9 – 12).

There have been extensive studies of NHC ligands at a variety of theory levels [14]. Additionally, numerous computational studies of Schrock- and Fischer-type TM carbenes have appeared in the literature [15]. The seminal computational work on TM-carbenes is that of Taylor and Hall who discriminated the bonding in Fischer and Schrock carbene complexes as resulting from singlet and triplet coupling, respectively, of carbenes to the metal functionality [16]. Subsequent ab initio studies by Cundari and Gordon suggest that the description of the metal-carbon linkage is a linear combination of more than two resonance structures, some of which were not previously considered [17].

To our knowledge, a systematic and comprehensive study of NHC complexes, particularly those of the late transition metals, has not been reported. Herrmann and coworkers have reported an elegant electronic structural analysis of Group 6 NHCs using a combination of theory (density functional methods) and experiment (high precision X-ray crystallography) [18]. Boehme and Frenking have addressed the bonding in NHC complexes of CuCl, AgCl, and AuCl with Møller-Plesset second order perturbation theory [19]. They also compared and contrasted NHCs to their silicon and germanium congeners. Density functional calculations have been successfully employed to study the chemistry of NHC complexes of platinum and their “abnormal” (arising from H transfer to the carbene carbon) isomers [20]. As a contribution to the aforementioned TM-NHC literature, this paper reports a combined crystallographic and computational chemistry study of NHC complexes of the late transition metals. Attention is focused on the response of the late TM-NHC linkage to modification of the metal.

CHAPTER 2

COMPUTATIONAL METHODS

Calculations were performed with the Gaussian98 [21] package. *Ab initio* calculations utilized the Stevens effective core potentials (ECPs) and attendant valence basis sets (VBSs) [22]. This scheme, dubbed CEP-31G(d), entails a valence triplet zeta description for the transition metals, a double-zeta-plus-polarization basis set for main group elements, and the -31G basis set for hydrogen. Tests were carried out with extended basis sets, e.g., f polarization functions on the metal, diffuse functions on main group elements, and small differences in calculated properties observed. The CEP-31G(d) ECP/VBS combination was used in concert with wavefunction (restricted Hartree Fock (RHF), Møller-Plesset second order perturbation (MP2), multiconfiguration self consistent field (MCSCF)) and density functional theories. Several pure and hybrid density functionals were investigated. The various methods researched were found to yield similar calculated results. Hence, the results reported herein are for the B3LYP functional [23] due to the reduced cost of DFT versus correlated post-Hartree-Fock methods.

The natural bond orbital (NBO) analysis [24] was used for studying the electronic structure of the late transition metal N-heterocyclic carbenes (NHCs) optimized at the B3LYP/CEP-31G(d) level of theory.

The Cambridge Structural Database (CSD) [25] was mined for a variety of transition metal complexes. Search refinements were employed to focus on the most reliable crystal structures. Structures subsequent to search refinement cannot be ionic,

disordered, contain reported errors, or possess polymeric linkages. Additionally, the R value must be less than 10%.

CHAPTER 3

RESULTS AND DISCUSSION

Comparison of M-NHC and Metal-Alkyl Bonds

To first assess the nature of the metal-carbon linkage in N-heterocyclic carbene (NHC) complexes the geometry about the carbene carbon was investigated in the Cambridge Structural Database (CSD). For the $\text{TM}_{\text{late}}=\text{NHC}$ entities the sum of the angles at the carbene carbon was tabulated as well as the $\text{M}=\text{C}-\text{A}_3\cdots\text{A}_4$ improper torsion ($\text{A}_{3,4}$ are substituent atoms for the carbene carbon). The former should be 360° and the latter 180° for a perfectly planar carbon atom. The averages for the $\text{TM}_{\text{late}}=\text{C}$ complexes in the CSD are 359.7° and 176.4° , respectively, for the sum of the angles and improper torsion at the carbene carbon, suggesting a planar carbon and the potential for metal-carbon multiple bonding.

A search of the CSD was performed for complexes designated as having a “double bond” between a late transition metal (i.e., from the Co-, Ni-, Cu- and Zn-triads) and a three-coordinate carbon, the majority of which possess NHC ligands. Examples designated as carbenes were found for 11 of 12 late transition metals with cadmium being the only exception. The average $\text{M}=\text{C}$ bond lengths are organized in Table 1. A complementary CSD search was conducted for $\text{M}-\text{C}$ (four coordinate) complexes, and the $\text{M}-\text{C}$ distances tabulated, Table 1. The $\text{M}=\text{C}/\text{M}-\text{C}$ ratio was calculated for each of the 11 metals for which data were available.

Table 1. Late Transition Metal Carbenes and Alkyl Bond Lengths (in Å)^a

Metal	Ave	#	Ave	#	Bond
	M=C	M=C	M-C	M-C	Ratio
Ag	2.07	2	2.17	23	0.95
Au	2.00	22	2.09	256	0.96
Co	1.92	13	1.98	722	0.97
Cu	1.88	2	2.00	58	0.94
Hg	2.09	4	2.10	146	1.00
Ir	1.94	16	2.14	156	0.91
Ni	1.89	20	1.96	154	0.96
Pd	1.99	11	2.07	439	0.96
Pt	1.98	23	2.08	877	0.95
Rh	1.97	17	2.10	223	0.94
Zn	2.01	1	2.00	214	1.01
Ave					0.96

^a Metal-carbon bond lengths obtained from the Cambridge Structural Database [24]; ‘Ave M=C’ is the average metal-carbon “double” bond length for NHC complexes; ‘# M=C’ is the number of metal-NHC samples found in the CSD; ‘Ave M-C’ is the average metal-carbon single bond length for alkyl complexes; ‘# M-C’ is the # of metal-alkyl samples in the CSD; ‘Bond Ratio’ is ‘Ave M=C’ divided by ‘Ave M-C.’

The average M=C/M-C ratio is 0.96 for the late transition metals, indicating an average 4% shortening upon going from a single to “double” bond. This is much less than the $\approx 14\%$ shortening seen for examples involving the light main group elements,

e.g., C-C $\rightarrow$ C=C. In experimental [26] and theoretical [27] studies of Group IVB chalcogenidos ($L_nM=Ch$, Ch = O, S, Se, Te) bond shortenings upon going from M-ChR $\rightarrow$ M=Ch ranged from 10% (Ch = O) to 5% (Ch = Te).

Of the experimentally derived M=C/M-C ratios for late transition metals the greatest shortenings are seen for the two Group 9 metals, i.e., those to the furthest right among those studied: rhodium (6% shortening) and iridium (9% shortening). Copper also has an average M=C/M-C ratio of 0.94, although this is based on only two Cu=NHC examples.

Another database search of complexes was performed for the non-late TM(=CX₂)(-CX₃) (X = any atom) motif. Searching for single and double bonds within the same complex should minimize variations in metal-carbon bond lengths arising from differences in formal oxidation state or coordination number. The data was organized by triad. Sufficient examples ($n > 3$) were found for the Group 5 through Group 8 metals, and indicate a greater shortening than is seen for the late TM-NHC complexes: %shortening = 12% (Group 5, $n = 12$), 13% (Group 6, $n = 34$), 11% (Group 7, $n = 5$) and 6% (Group 8, $n = 8$). It is interesting to note that the percentage shortening upon going from a M-C to M=C bond is greatest for the Cr triad, and decreases markedly for the Fe-triad. Thus, taken together, analysis of the crystallographic data suggest minimal metal-carbon bond shortening for TM_{late}=NHC complexes versus comparable TM_{late}-alkyl complexes.

Change in Geometry Upon Coordination

The geometries of free, non-coordinated NHCs were compared to those of ligated NHCs to see if any significant changes took place upon its coordination to the metal. The

values obtained are shown in Scheme 6, and are based on 13 examples for metal-free NHCs and 156 samples for NHC complexes. It is apparent from the data in Scheme 6 (values for metal-NHC complexes in italics/bottom, Scheme 7) that there is little change in the NHC ligand upon coordination to the metal. Note the disparity in length among the three different N---C bond lengths: $C_a-N > C_b-N > C_c-N$.

Scheme 7. Computational geometrical structure comparison of the NHC ligands, uncoordinated and ligated to the transition metals.

A B3LYP/CEP-31G(d) geometry optimization of $C_3N_2Me_2H_2$ yields $C_a-N = 1.46$ Å, $C_b-N = 1.40$ Å, and $C_c-N = 1.39$ Å, in splendid agreement with experimental values for complexed and uncomplexed NHCs. The calculated NBO bond orders are $C_a-N = 0.99$, $C_b-N = 0.97$ Å, and $C_c-N = 1.36$. The different C-N σ bonds are each polarized towards N, in roughly a 2:1 ratio. Interestingly, the hybridization of the lone pair on the divalent carbon is almost nearly perfectly sp . The populations of the $p\pi$ orbitals are $1.58 e^-$ for each nitrogen and $0.63 e^-$ for the divalent carbon. The calculated NBO charges are $N^{-0.49}$, divalent $C^{+0.15}$ and alkene $C^{-0.05}$.

The NBO analysis of NHCs is consistent with resonance between the two equivalent structures in Scheme 8. This description of the NHC ligand suggests a substantial contribution from resonance structures B and C in the NHC complexes, Scheme 9.

Scheme 8. NBO analysis representation of NHC ligand.

Scheme 9. Representations of different possible resonance contributors from the NHC ligand.

The NBO and structural analyses suggest that the C-N bonds in the NHCs are intermediate between single and double bond values. To put the measured values for NHCs into an appropriate context several CSD searches were conducted for prototypical carbon-nitrogen single and double bonds (X = any atom), Scheme 10.

Scheme 10. Geometry of the CSD search query for carbon-nitrogen bonds.

These searches were divided into two classes: organic C-N compounds (Z = non-metal in Scheme 10), and metal complexes (Z = transition metal in Scheme 10) with C-N ligands (except cyanide). Average bond lengths (in Å) for single and double carbon-nitrogen bonds were as follows: 1.48 (C-N organic; n = 3657); 1.29 (C=N organic; n = 786); 1.44 (C-N complexed; n = 25); 1.26 (C=N complexed; n = 153). Variation in the metal center had no appreciable effect on the carbon-nitrogen bond lengths in complexed systems, including NHCs.

The above values, combined with bond lengths for carbon-nitrogen triple bonds (searching for X-C≡N), were used to relate C-N bond length to bond order, as per Pauling [27]. The resulting equation

$$R_{\text{CN}} = -0.3011 * \ln(\text{BO}_{\text{CN}}) + 1.482$$

was used to calculate C-N bond orders in a series of compounds. Calculated bond orders based on the CSD average for NHC complexes, see Scheme 7, were 1.50 (N-C_c); 1.27 (N-C_b); 1.11 (N-C_a). Other carbon-nitrogen bonds have bond orders estimated from the above equation of 1.89 (organic C=N); 1.62 (pyridine [29]); 1.01 (organic C-N). The NBO and structural analyses suggest that a third resonance structure also plays an important role in the chemistry of the NHC ligand, Scheme 10. Rough estimates place the distribution between the two equivalent structures in Scheme 8 and that in Scheme 11 as 80%:20%.

Scheme 11. Another NBO representation of the NHC ligand, showing the $2e^-$ donor site/

Effect of Carbon Hybridization

It is clear from the data in Table 1 that the M-C bond shortening upon going from alkyl to carbene is substantially less in percentage terms for late transition metals than that seen for carbene complexes of the early to middle transition metals. Two origins for the shortening in late TM-NHC complexes immediately suggest themselves: (a) multiple bonding character in the metal-carbon linkage, and/or (b) a change in hybridization from sp^3 to sp^2 (as might be expected from the coordination environment of the divalent carbon) or sp (as suggested by the NBO analysis). To investigate this further using the Cambridge database, a search was conducted for metal-acetylide (M-C(sp), X=H, Me, Cl, PMe_3 , CMe_3 , $SiMe_3$, Ph) and metal-vinyl (M-C(sp^2), 3-methyl-2-buten-2-yl) fragments, Schemes 12 and 13.

Scheme 12. Possible resonance contributors to the geometry of the vinyl complexes.

Scheme 13. Possible resonance contributors to the geometry of the acetylide complexes.

The average metal-carbon bond lengths for the late transition metal-acetylides and vinyl are statistically indistinguishable from those for late TM-NHCs, Table 2. Indexed relative to the “M=C” bond length of the NHC complexes, the average bond ratios obtained from the CSD are 1.00 ± 0.02 (M=C/M-acetylide) and 0.98 ± 0.02 (M=C/M-vinyl).

NBO calculations were carried out on optimized acetylide and vinyl complexes, with special attention given to the metal-carbon bonds. Analysis of these complexes depicts metals and carbons as singly bound to each other, with a bond order less than one, 0.77 for vinyl and 0.75 for acetylide complexes. Three of the resonance structures for the acetylide and vinyl complexes are shown in Schemes 12 and 13. The NBO analysis supports a combination of structures 12a, 13a (singly bonded) and 12c, 13c (dative).

Table 2. Metal-Carbon Bond Lengths for Vinyl and Acetylide Complexes.^b

Metal	M- acetylide	stdev	n	M- vinyl	stdev	n
Au	2.03	0.03	31	2.03	n/a	1
Co	1.88	0.03	7	1.95	0.04	9
Hg	2.01	0.02	32	2.06	0.03	14
Ir	2.01	0.03	10	2.03	0.04	11
Ni	1.85	0.01	14	1.89	0.02	8
Pd	2.00	0.05	12	2.00	0.02	7
Pt	2.00	0.04	43	1.99	0.19	17
Rh	2.00	0.03	15	2.06	0.06	13
Mo	2.18	0.05	3	2.24	0.02	5
W	2.12	0.04	9	2.28	0.02	5
Ta	2.18	0.01	3	2.20	0.08	3
Cr	n/a	n/a	0	2.07	0.05	6

^b Metal-carbon bond lengths obtained from the Cambridge Structural Database;²⁴ ‘M-acetylide’ is the average metal-carbon bond length for the metal-acetylide complexes; ‘M-vinyl’ is the average metal-carbon bond length for the metal-vinyl complexes; ‘stdev’ is the standard deviation obtained from the complexes studied; ‘n’ is the number of metal-acetylide or vinyl samples found in the CSD.

Analysis of the vinyl, acetylide and alkyl complexes support the existence of metal-carbon single bond. For the vinyl complexes analyzed, the average C₁-C₂-C₃ angle matches that of an sp² hybridized C₂ carbon, with a value of 121±3°. Angle analyses for

the acetylide complexes show no change from sp hybridization at the C₂ carbon, with an average C₁-C₂-X₃ angle of 179±1°, indicative of 12a as the lead configuration. The sum of the TM-C-H angles in the metal-alkyl complexes theoretically would equal 328.5° if the carbene carbons were perfectly tetrahedral. Analysis shows a total of 330±3°, consistent with a sp³ hybridized alkyl carbon. Based on their similarity, if vinyls, acetylides and alkyls exhibit predominant metal-carbon single bond character whilst bound to the metal, it is reasonable to conclude that TM-NHCs exhibit single bond character.

Natural Bond Order Analyses

Natural bond order analyses were carried out on a collection of NHC complexes incorporating a variety of late transition metals and geometries (linear/two-coordinate; square planar/four-coordinate; tetrahedral/four-coordinate; octahedral/six-coordinate), which correspond to the most prevalent coordination environments for NHC complexes. Also, NBO analyses were conducted on a variety of TM-vinyl/acetylide/alkyl complexes to obtain cooperative information about their metal-carbon bonds. Representative examples of the NHC complexes studied are shown in A-1; a complete list of target molecules is given in A-2-4. The parent NHC ligand C₃N₂H₄ is used for the calculation of all TM-NHC complexes and structures similar to those shown in Schemes 12, 13 and 14 were used for vinyl, acetylide and alkyl complexes, respectively.

Scheme 14. Representative structure of the alkyl complexes studied.

Starting geometries are obtained from the appropriate crystal structure and optimized at the B3LYP/CEP-31G(d) level of theory before the NBO analysis is performed at the optimized stationary point at this same level of theory. The NBO results are remarkably consistent across the series of complexes studied. The most stable resonance structure of the TM-NHC complexes, 15c, results from the two localized representations 15a and 15b. From the NBO analysis, an average bond order of 0.78 was obtained for the TM-NHC samples studied suggesting a metal-carbon single bond with substantial ionic/dative character. Similar to the NHCs, the vinyl, acetylide, and alkyl complexes show bond orders approximately 0.77, further supporting the single bond nature of the bond between the TMs and NHCs.

Scheme 15. NBO resonance representations of NHC-TM complexes.

The natural charge obtained from NBO for the carbene carbon averaged to +0.22. Each nitrogen's natural charge averages to -0.60. The average bond order for N-C_{carbene} bond is 1.34, suggesting a partial double bond character spanning over the N-C-N substructure as depicted in Scheme 15c. Hybridization for the carbene carbon in the NHC complexes (ave. p:s ratio = 1.57) is intermediate between sp² (ave. p:s ratio for vinyl complexes = 2.94) and sp (ave. p:s ratio for acetylide complexes = 1.03) as portrayed by the NBO calculations, thus possessing considerably more s character than

an sp^3 hybridized alkyl carbon (ave. p:s ratio for alkyl complexes = 3.27), causing the observed metal-carbon bond shortening in NHC complexes.

It can be proposed that given that the metal-carbene carbon bond possesses substantial dative/ionic character, the NHC ligand possesses substantial trans influence. Further investigation of this property was carried out on the two TM-NHC complexes seen in Scheme 16 (BABNIC: 16a; modified BABNIC: 16b). Total electron density plots with a 0.09 isodensity value show the metal-ligand interaction. The electron density of 15a is consistent with its NBO analysis. The presence of a NHC ligand trans to a phosphine ligand causes electron density depletion around the metal-phosphorous bond, relative to the metal-carbene carbon bond. NBO analysis describes the phosphorous with an extra lone pair and carbene carbon as bound to the transition metal. Structure 10b is also consistent with the NBO analysis, where the carbonyl trans to the NHC causes an electron density diminution around the metal-carbene carbon. TM-NHC complexes hence illustrate a dative interaction between metals and carbene carbons, explaining the average bond order of 0.78 for the examples analyzed.

(a)

(b)

Scheme 16. Total density plot showing the NHC's trans effect.

CHAPTER 4

SUMMARY AND CONCLUSIONS

N-heterocyclic carbenes (NHCs) have proven useful as phosphine equivalents in many instances, as exemplified by the works of Arduengo and others. They comprise a third family of carbene complexes in addition to the Fischer and Schrock types. A small number of transition metal (TM)-NHC complexes have been studied computationally but not enough data exists particularly for complexes of metals in groups 9-12. This study of TM-NHC complexes allowed for several significant conclusions, the most important of which are summarized below.

The metal-carbene carbon bond between TMs and ligated NHCs is on average 4% shorter than the average metal-carbon bond. This research investigated two hypotheses explaining the bond shortening: 1) multiple bond character; 2) hybridization at the NHC carbene carbon. Analysis of CSD-obtained non-ligated NHCs compared to ligated ones show very little change upon coordination, implying that the bond shortening does not occur due to a geometry modification. Indexed relative to TM-vinyls/acetylides, the metal-carbon bond lengths of TM-NHCs are practically indistinguishable suggesting a possible sp^2 or sp hybridization for the NHC carbene carbon.

Natural bond order (NBO) calculations on TM-vinyl/acetylide/alkyl complexes reveal metal-carbon bond orders less than one, similar to TM-NHC complexes. The hypothetical presence of a metal-carbon double bond for TM-NHC complexes did not fit the data obtained from the optimized vinyl, acetylide and alkyl complexes. The similarity of the results with NBO analyses of TM-NHC complexes suggested a metal-carbene

carbon single bond for the TM-NHC complexes. Additional investigations of the TM-NHC complexes reveal NHC ligands bind to TMs with substantial dative/electrostatic character. Total electron density plots illustrate this property in conjunction with ligands trans to the NHCs. Also, bond order trends across the periodic table for TM-NHC complexes reveal that the metal-carbene carbon bond possesses substantial ionic character with a considerable trans influence.

APPENDIX

A-1 Model N-heterocyclic carbene complexes studied in this research. The six-letter reference code from the Cambridge Crystallographic Database is given in A-5.

BABNIC

BICZUI

CECZEP

CPIMPT

FIGDOO

GUGVEJ

NOHKIE

PEPPIM20

PIYBAA

PIYBEE

PUMYAX

REJTEF

TUCSUF

TUCTAM

ZOFXEX

A-2. Model vinyl complexes studied in this research. The six-letter reference code from the Cambridge Crystallographic Database is given in A-5.

BAZHAL

CAPDAY

CICDUN

DAMLOS10

DUNBOD

FIPHIV

GUKHOJ

JEPPID

JOGSAZ

QAXCUN

XAWLUC

A-3. Model alkyl complexes studied in this research. The six-letter reference code from the Cambridge Crystallographic Database is given in A-5.

ACEFOD

ACESIK

ACESOQ

ACEWEK

ADEYOX

BAHWOW

BEFKIG

BODRER

CEHTIS

COWKOO

DMCPHF

GUQWOE

HAFDUN

HOPNOP

JECJEG

JETHEV

KELQEX

LAMTAU

LEKFEM

LOJDIX

A-4. Model acetylide complexes studied in this research. The six-letter reference code from the Cambridge Crystallographic Database is given in A-5.

BAXGEM

BONSUS

CAMJEF

CPFPEY

CUBRIA

DAVRAT

DAXWOO

DUZYUS

GINTOM

IBINOW

JAYMAX

JIKXUW

KEQVIL

MEVHOK

MIWWUK

NAKJOY

PASTEI

PEEPNI

PETXER

QEWZOH

RABVUH

WEKMUU

XAKYAJ

ZEGYEP

A-5. The six-letter reference code from the Cambridge Crystallographic Database.

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