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Rhodium and Iridium Complexes of N-Heterocyclic Carbenes via Transmetalation: Structure and Dynamics

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Rhodium and iridium complexes of N-heterocyclic carbenes (**3a**−**c** and **4a**−**c)** were obtained by transmetalation from the corresponding Ag(I) complexes. The structure of **3b** was verified by X-ray diffraction. The compounds display restricted rotation about the metal−carbene bond, the rate of which can be controlled by altering the steric bulk of the auxiliary ligands. Infrared spectroscopy provides an estimate of the electron-donor power of the carbene ligands from ν(CO) of the carbonyl derivatives.

Introduction

N-heterocyclic carbenes (NHCs)[1−3] are an increasingly useful class of ligands in transition-metal compounds. Since the concurrent reports of the first metal−NHC complexes in 1968 by Öfele[4] and by Wanzlick and Schönherr[5] and the isolation of the first stable free carbenes in 1991 by Arduengo et al.,[6] many catalyst systems with NHC spectator ligands have been described.[7−10] Because of their strong binding and low reactivity, NHCs are often compared to phosphine ligands. Substantial differences between NHCs and PR_3 seem to exist, however, notably in the electron-donor power of the ligands. The ligand precursors, disubstituted imidazolium salts, are straightforward to make,[1,10−13] but preparation of metal compounds from these salts can be more difficult. The most common method is direct complexation of the free NHC, either isolated[14] or generated in situ,[8,15] formed by deprotonation of the imidazolium salt. These methods require that the free NHC be stable (at least transiently) and may be fatally complicated by the presence of other acidic protons in the ligand precursor. The imidazolium salt may also be deprotonated by a basic ligand on the metal reactant.[9,16,17] Oxidative addition of a 2-haloimidazolium carbon−halogen bond[18] or of an imidazolium carbon−hydrogen bond[18,19] to a low-valent metal center and addition of an electron-rich olefin with $\mathrm{C{=}C}$ bond cleavage[20] can also lead to metal−NHC complexes in certain cases. A number of metal−NHC compounds have been prepared by transmetalation from lithiated azoles, most notably thiazoles, followed by protonation or alkylation of the resulting anionic heteroaryl ligand

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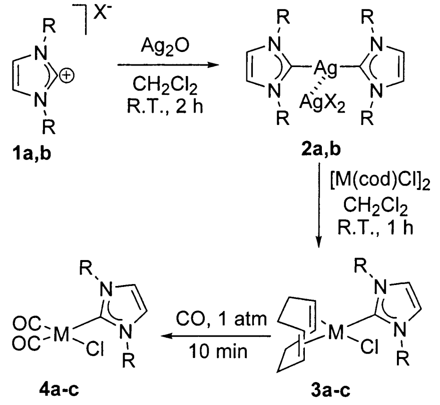
to form the carbene.[21] Because of the lack of generality of current synthetic strategies, it is important to develop a wider variety of routes to metal−NHC complexes.

The promising silver transmetalation method of Wang and Lin was introduced in 1998.[22] A wide variety of silver−NHC complexes have been synthesized,[13,23] and many of these NHC ligands have been successfully transferred to palladium[12,24,25] and gold.[22] To our knowledge, this method has not been applied to other transition metals, although related transmetalations of saturated imidazolidin-2-ylidene ligands from Cr, Mo, and W to a variety of late metals have been achieved.[26] We report here the facile syntheses of rhodium and iridium complexes of NHCs by transfer from the corresponding silver−carbene complexes. We find that the iridium and rhodium complexes show hindered rotation about the metal−NHC bond. Where possible, the activation free energy of rotation was determined. As previous studies[27−30] have indicated, the barrier to rotation seems to be largely steric in nature, because the carbene M−C bond is essentially single. Syntheses of carbonyl derivatives allowed us to estimate the electron donor character of the NHCs. The results corroborate previous studies,[16,31] which suggest that NHCs are very strongly donating ligands, even more so than trialkylphosphines.

Results and Discussion

Synthesis and Characterization. The compounds Rh(cod)Cl(tmiy) (**3a**; cod = (1,2,5,6-η)-1,5-cyclooctadiene, tmiy = 1,3-bis(4-tolylmethyl)imidazolin-2-ylidene), Ir(cod)Cl(tmiy) (**3b**), and Ir(cod)Cl(biy) (**3c**), (biy = 1,3-dibutylimidazolin-2-ylidene) were synthesized as shown in Scheme 1. The symmetrically disubstituted imidazolium salts **1a**,**b**[32] were treated with Ag$_2$O at room temperature to form the corresponding silver−carbene compounds **2a**,**b**, respectively. Silver−carbene complexes of this type are known to have a variety of different structures in the solid state,[13,22,25] and a solution equilibrium between Ag(carbene)X and Ag(carbene)$_2^+$ species has been proposed.[22] The structural formula shown is consistent with NMR and microanalytical data, but the formulation Ag(carbene)Cl is also possible. No Ag−C coupling was observed in the ^{13}C NMR, consistent with equilibration in solution.

Scheme 1. Synthesis of Rhodium− and Iridium−NHC Compounds Using Transmetalation from Silver



1a, 2a: R = 4-tolylmethyl, X = Cl
1b, 2b: R = butyl, X = Br
3a, 4a: R = 4-tolylmethyl, M = Rh
3b, 4b: R = 4-tolylmethyl, M = Ir
3c, 4c: R = butyl, M = Ir

Reaction of **2a**,**b** with [Rh(cod)Cl]$_2$ or [Ir(cod)Cl]$_2$ at room temperature readily gave the yellow metal−carbene compounds **3a**−**c**. Similar compounds have been prepared using a base in situ.[16,33] Attempts to prepare iridium−bis(carbene) compounds from either [Ir(cod)Cl]$_2$ or **3b** using additional silver−carbene and AgPF$_6$ or NaPF$_6$ to abstract the chloride ligand were unsuccessful.

The compounds **3a**−**c** were converted to the corresponding dicarbonyl compounds **4a**−**c** with CO (1 atm) in methylene chloride at room temperature. Cyclooctadiene is easily displaced in minutes, as shown by a color change from bright to pale yellow. The cis geometry proposed in Scheme 1 is supported by IR spectroscopy, which shows two CO stretching vibrations of similar intensity. Inequivalent CO carbon atoms can also be observed by ^{13}C NMR spectroscopy. The cis geometry is consistent with the ^{1}H NMR spectrum, in which the N−CH$_2$ protons are diastereotopic, e.g., in **3a**−**c**.

Structural Study. The structure of compound **3b** was determined using single-crystal X-ray diffraction (Figure 1); selected bond lengths and angles are shown in Table 1. The coordination is square planar at the iridium(I) center. As is expected for NHCs, the C$_{\text{carbene}}$−Ir bond length of 2.029(4) Å suggests a single bond. The C(2)−C(3) distance of 1.340(7) Å in the imidazole ring is consistent with a double bond and supports the perturbed aromatization[2] proposed to occur upon carbene formation. The mean C$_{\text{cod}}$−Ir distance is 2.104(8) Å trans to chlorine and 2.188(8) Å trans to the NHC.

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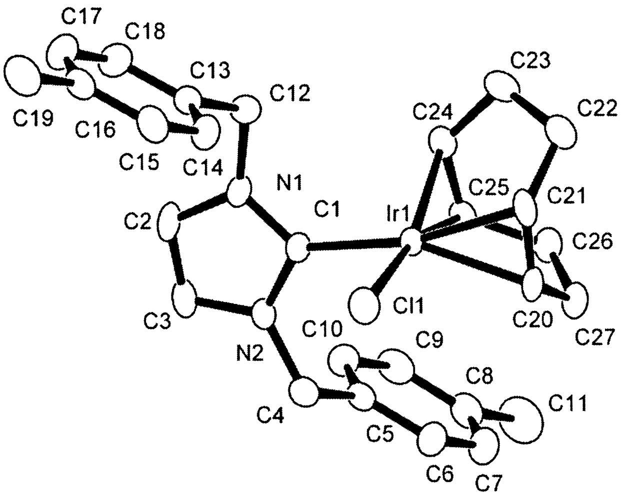


Figure 1. ORTEP diagram of **3b**, showing 50% probability ellipsoids.

Table 1. Selected Bond Lengths and Angles for 3b

Bond Lengths (Å)			
Ir(1)−C(1)	2.029(4)	Ir(1)−C(24)	2.102(4)
Ir(1)−Cl(1)	2.363(1)	Ir(1)−C(25)	2.105(4)
Ir(1)−C(20)	2.175(4)	C(2)−C(3)	1.340(7)
Ir(1)−C(21)	2.200(4)		
Bond Angles (deg)			
C(1)−Ir(1)−C(20)	156.2(2)	Cl(1)−Ir(1)−C(21)	92.0(1)
C(1)−Ir(1)−C(21)	166.7(2)	Cl(1)−Ir(1)−C(24)	155.7(1)
C(1)−Ir(1)−C(24)	93.0(2)	Cl(1)−Ir(1)−C(25)	165.2(1)
C(1)−Ir(1)−C(25)	93.6(2)	N(1)−C(1)−N(2)	104.0(4)
C(1)−Ir(1)−Cl(1)	88.0(1)	N(1)−C(1)−Ir(1)	130.6(3)
Cl(1)−Ir(1)−C(20)	91.4(1)	N(2)−C(1)−Ir(1)	125.3(3)
Torsional Angles (deg)			
N(1)−C(1)−Ir(1)−Cl(1)	97.5(4)		
N(2)−C(1)−Ir(1)−Cl(1)	−79.9(4)		

Table 2. Rate Constants and Activation Free Energies for Metal−Carbene Bond Rotation at 35 °C

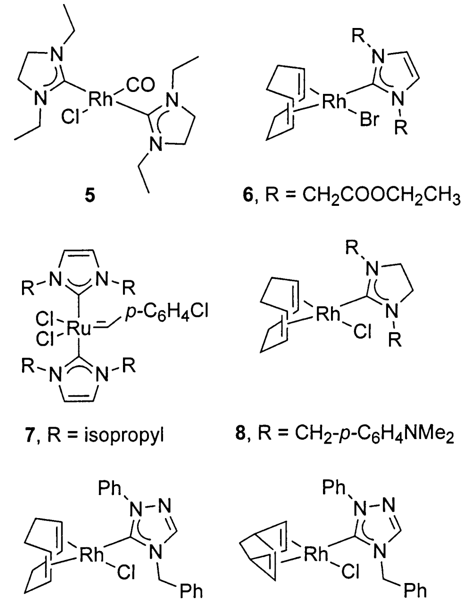
compd	k_{rotation} (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
4a	9.2	16.7
4b	48	15.7

The difference of 0.08(1) Å results from the much higher trans influence of the carbene ligand. The torsional angles for N−C−Ir−Cl indicate that the imidazole ring is almost orthogonal to the square plane, which accounts for the diastereotopic N−CH_2 protons if Ir−C rotation is slow.

Variable-Temperature ^{1}H NMR Studies. At room temperature, compounds **3a**−**c** show a sharp AB pattern (**3a**,**b**) or an ABXY pattern (**3c**) for the diastereotopic N−CH_2 protons in the ^{1}H NMR spectrum, indicating that there is no rotation about the carbene−metal bond on the NMR time scale. Spectra taken up to +105 °C in toluene-d_8 show no broadening of these peaks. This is consistent with a free energy barrier of >22 kcal/mol for M−C bond rotation. Compounds **4a**−**c**, in contrast, are fluxional. Compounds **4a**,**b** show a sharp AB pattern for the benzylic protons at 0 °C. As the temperature is increased, the peaks broaden and coalesce into a singlet at about 55 °C, indicating rotation about the M−C bond. Line shape analysis gave rate constants and activation free energies for rotation at 35 °C (Table 2).

Our data agree well with those of Doyle and Lappert[26] on the imidazolidine **5** (Chart 1), where $\Delta G^{\ddagger}$ is 16 kcal/mol. The steric environment of the Rh−C bond is similar to that in compound **4a**, in that the ligands cis to the NHC are CO and chloride, and the N substituents are of the form −CH_2R. Previous studies have strongly indicated that no electronic rotation barrier exists for the NHCs. For example, the sterically crowded compounds **6**,[28] **7**,[29] and **8**[34] have been shown to exhibit no M−C rotation at room temperature. Studies by Enders and Gielen[30] on **9** and **10** directly support a steric origin of the rotation barrier, because compound **9** shows no rotation at room temperature, while **10** (and **4a**) have a lower barrier. The steric barrier to rotation fits as well for compounds **4a**−**c** compared to **3a**−**c**.

Chart 1. Compounds Known To Exhibit Hindered M−C_{carbene} Bond Rotation



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6, R = $CH_2COOCH_2CH_3$

7, R = isopropyl

8, R = CH_2-*p*-$C_6H_4NMe_2$

9

10

Table 3. Carbonyl Stretching Frequencies for Compounds $Ir(CO)_2Cl(L)$

L	solvent	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})	TEP (cm^{-1})
tmiy (**4b**)	CH_2Cl_2	2063, 1976	2020	2050[a]
biy (**4c**)	CH_2Cl_2	2062, 1978	2020	2051[a]
PCy_3	CH_2Cl_2	2072, 1984	2028	2056.4
P^iPr_3	CH_2Cl_2	2077, 1986	2032	2059.2
PEt_3	$CHCl_3$	2081, 1994	2038	2061.7
$P(p\text{-}CH_3C_6H_4)_3$	$CHCl_3$	2079, 1999	2039	2066.7
PMe_2Ph	$CHCl_3$	2084, 1999	2042	2065.3
PPh_3	$CHCl_3$	2085, 2002	2044	2068.9
$P(OBu)_3$	CS_2	2084, 2003	2044	2077
$PMePh_2$	$CHCl_3$	2085, 2003	2044	2067
$P(OPh)_3$	$CHCl_3$	2089, 2009	2049	2085.3

[a] Values are calculated using linear regression with L = $P(OBu)_3$, $P(OPh)_3$ excluded.

Infrared Spectroscopy. The CO compounds **4b**,**c**, studied using FT-IR spectroscopy, gave the ν(CO) data shown in Table 3. The known values for structurally analogous phosphine compounds, $Ir(CO)_2ClPR_3$, are given.[35] A plot (Figure 2) of the average ν(CO) value for these compounds versus the Tolman electronic param-

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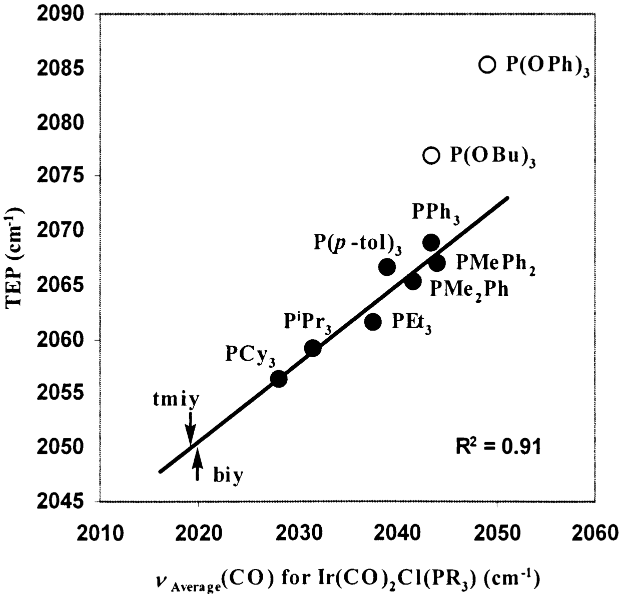

Figure 2. Correlation of the average ν(CO) values for compounds $Ir(CO)_2ClL$ with the Tolman electronic parameters (TEP). The regression line shown excludes L = $P(OBu)_3$, $P(OPh)_3$. Extrapolated positions of the NHC ligands studied are indicated by arrows.

eter (TEP)[36] shows a good linear correlation ($R^2 = 0.91$) if the phosphite ligands are excluded. As significant π-acceptors, the TEP values of phosphites are likely to depend more on the nature of the metal than for the essentially single-bonded $R_3P{-}M$ and carbene−M systems, which are more readily comparable. Because weak π-acceptor PR_3 and carbene ligands give a good correlation, the TEP values for the NHCs studied can be estimated using the linear regression equation TEP = $0.722[\nu_{\text{average}}(CO)] + 593\ \text{cm}^{-1}$. This provides a convenient experimental method for evaluating the electronic character of NHC ligands.

The IR data indicate that the NHCs studied are more electron-donating than even the most donating phosphine ligands. The same conclusion was reached in a qualitative comparison of IR data for a rhodium−NHC compound by Nolan and co-workers[37] and in our own computational study.[38] In a calorimetric study of the formation of ruthenium−NHC compounds, Nolan and co-workers[31] found that ΔH was more negative than for the formation of the corresponding PCy_3 compound, suggesting that the carbene ligands are more tightly binding.

Conclusion

Transmetalation from silver is applied for the first time to the synthesis of rhodium− and iridium−NHC compounds. They show a steric barrier to metal−carbene bond rotation, the magnitude of which can be controlled by adjusting the auxiliary ligands on the metal center. Carbonyl derivatives provide a convenient way to estimate Tolman electronic parameters for NHCs. The results reinforce the idea that N-heterocyclic carbenes are stronger electron donors than even the most basic phosphine ligands.

Experimental Section

General Methods. Substituted imidazolium salts[32a] and $[Ir(cod)Cl]_2$[32b] were synthesized as previously described. All subsequent syntheses were performed in air using reagent grade solvents, which were used as received. Isolated yields are given for all products. NMR spectra were recorded on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in parts per million, J in hertz). NMR spectra were obtained at room temperature unless otherwise noted. Assignments are based on HETCOR spectroscopy. Infrared spectra were recorded on a Midac FT-IR spectrometer, using NaCl plates. Elemental analyses were performed by Atlantic Microlab, Inc. Line shape analyses were performed using gNMR v4.1.

Bis[1,3-bis(4-tolylmethyl)imidazolin-2-ylidene]silver Dichloroargentate (2a). In a modification of the procedure of Wang and Lin,[22] 1,3-bis(4-tolylmethyl)imidazolium chloride (0.308 g, 0.983 mmol) and silver oxide (0.114 g, 0.491 mmol) were added to CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 2 h and filtered through Celite. The solvent was removed in vacuo at room temperature to give white crystals, which were washed with pentane (3 × 5 mL) and dried in vacuo. Yield: 0.397 g (95%). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.16 (m, 8H, H_{ar}), 6.90 (s, 2H, NCHCHN), 5.23 (s, 4H, CH_2), 2.34 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 138.9 (C_{ar}), 132.5 (C_{ar}), 130.0 (C_{ar}), 128.1 (C_{ar}), 121.6 (NCHCHN), 55.9 (NCH_2), 21.4 (CH_3). The Ag-bound carbon was not observed. Anal. Calcd for $C_{38}H_{40}Ag_2Cl_2N_4$ (839.32): C, 54.37; H, 4.80; N, 6.67. Found: C, 54.61; H, 4.84; N, 6.67.

Bis(1,3-dibutylimidazolin-2-ylidene)silver Dibromoargentate (2b). This was prepared in a manner analogous to that of **2a**, except that the compound was isolated as an oil and used immediately. A small amount of impurity was observable by NMR, and the product decomposed in purification attempts. Yield: 94%. ^{1}H NMR ($CDCl_3$, 298 K): δ 6.98 (s, 2H, NCHCHN), 4.08 (t, 4H, $^3J_{HH} = 7.4$ Hz, NCH_2), 1.78 (m, 4H, NCH_2CH_2), 1.33 (m, 4H, $NCH_2CH_2CH_2$), 0.94 (t, 6H, $^3J_{HH} = 7.4$ Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 298 K): δ 180.6 (NCAgN), 121.0 (NCHCHN), 52.0 (NCH_2), 33.7 (NCH_2CH_2), 19.9 ($NCH_2CH_2CH_2$), 13.9 ($NCH_2CH_2CH_2CH_3$).

[1,3-Bis(4-tolylmethyl)imidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chlororhodium (3a). $[Rh(cod)Cl]_2$ (0.413 g, 0.838 mmol) and **2a** (0.838 g, 0.838 mmol) were combined in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 1 h and filtered through Celite. The solution was concentrated in vacuo at room temperature. The yellow powder obtained was washed with pentane (3 × 5 mL) and dried in vacuo. Yield: 0.793 g (95%). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.28 (d, 4H, $^3J_{HH} = 7.7$ Hz, H_{ar}), 7.18 (d, 4H, $^3J_{HH} = 7.7$ Hz, H_{ar}), 6.64 (s, 2H, NCHCHN), 5.83 (d, 2H, $^2J_{HH} = 14.7$ Hz, NCH_2), 5.75 (d, 2H, $^2J_{HH} = 14.7$ Hz, NCH_2), 5.07 (m, 2H, CH_{cod}), 3.36 (m, 2H, CH_{cod}), 2.36 (s, 6H, CH_3), 2.33 (m, 4H, $(CH_2)_{cod}$), 1.91 (m, 4H, $(CH_2)_{cod}$). ^{13}C NMR ($CDCl_3$, 298 K): δ 183.3 (d, $^1J_{RhC} = 51.2$ Hz, NCRhN), 138.1 (C_{ar}), 133.7 (C_{ar}), 129.8 (C_{ar}), 128.4 (C_{ar}), 120.9 (NCHCHN), 99.0 (d, $^1J_{RhC} = 6.9$ Hz, CH_{cod}), 68.5 (d, $^1J_{RhC} = 14.8$ Hz, CH_{cod}), 54.6 (NCH_2), 33.1 ($(CH_2)_{cod}$), 29.1, ($(CH_2)_{cod}$), 21.4 (CH_3). Anal. Calcd for $C_{27}H_{32}ClRhN_2$ (522.93): C, 62.02; H, 6.17; N, 5.36. Found: C, 61.94; H, 6.22; N, 5.35.

[1,3-Bis(4-tolylmethyl)imidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium (3b). This compound was prepared in a manner analogous to that of **3a**, from $[Ir(cod)Cl]_2$ and **2a**. X-ray-quality crystals were grown by slow evaporation of CH_2Cl_2. Yield: 81%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.26 (d, 4H, $^3J_{HH} = 7.4$ Hz, H_{ar}), 7.18 (d, 4H, $^3J_{HH} = 7.4$ Hz, H_{ar}), 6.64 (s, 2H, NCHCHN), 5.71 (d, 2H, $^2J_{HH} = 14.7$ Hz,

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NCH_2), 5.59 (d, 2H, $^2J_{HH}$ = 14.7 Hz, NCH_2), 4.66 (m, 2H, CH_{cod}), 3.00 (m, 2H, CH_{cod}), 2.35 (s, 6H, CH_3), 2.18 (m, 4H, $(CH_2)_{cod}$), 1.74 (m, 2H, $(CH_2)_{cod}$), 1.57 (m, 2H, $(CH_2)_{cod}$). ^{13}C NMR ($CDCl_3$, 298 K): δ 180.9 (NCIrN), 138.1 (C_{ar}), 133.5 (C_{ar}), 129.8 (C_{ar}), 128.4 (C_{ar}), 120.5 (NCHCHN), 85.1 (CH_{cod}), 54.4 (NCH_2), 52.1 (CH_{cod}), 33.8 ($(CH_2)_{cod}$), 29.7 ($(CH_2)_{cod}$), 21.4 (CH_3). Anal. Calcd for $C_{27}H_{32}ClIrN_2$ (612.28): C, 52.96; H, 5.28; N, 4.58. Found: C, 53.06; H, 5.27; N, 4.56.

[(1,2,5,6-*η*)-1,5-Cyclooctadiene](1,3-dibutylimidazolin-2-ylidene)chloroiridium (3c). This compound was prepared in a manner analogous to that of **3a**, from $[Ir(cod)Cl]_2$ and **2b**. Yield: 68%. ^1H NMR ($CDCl_3$, 298 K): δ 6.84 (s, 2H, NCHCHN), 4.58 (m, 2H, CH_{cod}), 4.37 (t, 4H, $^3J_{HH}$ = 7.8 Hz, NCH_2), 2.93 (m, 2H, CH_{cod}), 2.20 (m, 4H, $(CH_2)_{cod}$), 1.94 (m, 2H, NCH_2CH_2), 1.78 (m, 2H, NCH_2CH_2), 1.73 (m, 2H, CH_{2cod}), 1.60 (m, 2H, $(CH_2)_{cod}$), 1.44 (m, 4H, $NCH_2CH_2CH_2$), 1.01 (t, 6H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$). The diastereotopic NCH_2 protons resonate as an ABXY pattern in toluene-d_8 but coincidentally overlap in $CDCl_3$. ^{13}C NMR ($CDCl_3$, 298 K): δ 179.9 (NCIrN), 120.1 (NCHCHN), 84.1 (CH_{cod}), 51.6 (CH_{cod}), 50.6 (NCH_2), 33.9 and 33.3 ($(CH_2)_{cod}$ and NCH_2CH_2), 29.8 ($(CH_2)_{cod}$), 20.3 ($NCH_2CH_2CH_2$), 14.0 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{19}H_{32}ClIrN_2$ (516.20): C, 44.21; H, 6.26; N, 5.43. Found: C, 43.92; H, 6.17; N, 5.33.

[1,3-Bis(4-tolylmethyl)imidazolin-2-ylidene]dicarbonylchlororhodium (4a). Compound **3a** (0.150 g, 0.287 mmol) was dissolved in CH_2Cl_2 (20 mL). CO gas was passed through the solution for 10 min. The solvent was slowly evaporated at room temperature. The pale yellow powder obtained was washed with pentane (3 × 5 mL) and dried in vacuo. Yield: 0.128 g (95%). ^1H NMR ($CDCl_3$, 298 K): δ 7.25 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{ar}), 7.19 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{ar}), 6.82 (s, 2H, NCHCHN), 5.55 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2), 5.43 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2), 2.34 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 185.6 (d, $^1J_{RhC}$ = 54.1 Hz, OCRh or NCRhN), 182.6 (d, $^1J_{RhC}$ = 74.6 Hz, OCRh or NCRhN), 174.7 (d, $^1J_{RhC}$ = 43.7 Hz, OCRh), 138.6 (C_{ar}), 132.7 (C_{ar}), 129.9 (C_{ar}), 128.5 (C_{ar}), 121.9 (NCHCHN), 55.1 (NCH_2), 21.4 (CH_3). FT-IR (CH_2Cl_2): ν(CO) 2076, 1995 cm^{-1} (similar intensities). Anal. Calcd for $C_{21}H_{20}ClRhN_2O_2$ (470.77): C, 53.58; H, 4.28; N, 5.95. Found: C, 53.56; H, 4.44; N, 5.95.

[1,3-Bis(4-tolylmethyl)imidazolin-2-ylidene]dicarbonylchloroiridium (4b). Compound **4b** was obtained in a manner similar to **4a**, from **3b**. Yield: 72%. ^1H NMR ($CDCl_3$, 298 K): δ 7.25 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{ar}), 7.20 (d, 4H, $^3J_{HH}$ = 8.0 Hz, H_{ar}), 6.82 (s, 2H, NCHCHN), 5.57 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2), 5.43 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2), 2.36 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 181.5 (NCIrN), 173.9 (OCIr), 168.2 (OCIr), 138.7 (C_{ar}), 132.4 (C_{ar}), 129.9 (C_{ar}), 128.5 (C_{ar}), 121.6 (NCHCHN), 55.0 (NCH_2), 21.4 (CH_3). FT-IR (CH_2Cl_2): ν(CO) 2063, 1976 cm^{-1}, similar intensities. Anal. Calcd for $C_{21}H_{20}ClIrN_2O_2$ (560.08): C, 45.03; H, 3.60; N, 5.00. Found: C, 44.89; H, 3.64; N, 5.10.

[1,3-Dibutylimidazolin-2-ylidene]dicarbonylchloroiridium (4c). This compound was prepared in a manner analogous to that of **4a**, except that **4c** is soluble in pentane and could not be washed. The cyclooctadiene byproduct was removed in vacuo over 3 days. Yield: 51%. ^1H NMR ($CDCl_3$, 298 K): δ 6.97 (s, 2H, NCHCHN), 4.36 (m, 2H, NCH_2), 4.17 (m, 2H, NCH_2), 1.86 (m, 4H, NCH_2CH_2), 1.40 (m, 4H, $NCH_2CH_2CH_2$), 0.98 (t, 6H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 298 K): δ 181.6 (NCIrN), 173.3 (OCIr), 168.3 (OCIr), 121.2 (NCHCHN), 51.3 (NCH_2), 32.9 (NCH_2CH_2), 19.4 ($NCH_2CH_2CH_2$), 13.9 ($NCH_2CH_2CH_2CH_3$). FT-IR (CH_2Cl_2): ν(CO) 2062, 1978 cm^{-1}, similar intensities. Anal. Calcd for $C_{13}H_{20}ClIrN_2O_2$ (463.99): C, 33.65; H, 4.34; N, 6.04. Found: C, 33.48; H, 4.37; N, 6.01.

Table 4. Crystallographic Data for 3b

color, shape	yellow plate
empirical formula	$C_{27}H_{32}ClIrN_2$
fw	612.24
radiation, λ (Å)	Mo Kα (monochr), 0.71069
T (°C)	−90
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimens	
a (Å)	10.6081(3)
b (Å)	10.7864(4)
c (Å)	11.3703(4)
α (deg)	88.061(2)
β (deg)	74.354(2)
γ (deg)	70.792(2)
V (Å^3)	1180.91(7)
Z	2
D_{calcd} (g cm^{-3})	1.722
μ(Mo Kα) (cm^{-1})	57.99
cryst size (mm)	0.05 × 0.07 × 0.12
total, unique no. of rflns	13 453, 5364
R_{int}	0.043
no. of params, restraints	280, 0
R,[a] R_w[b]	0.029, 0.034
GOF	0.81
min, max resid density (e Å^{-3})	−1.52, 0.69

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3.00\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Structure Determination and Refinement of 3b. Crystals suitable for study were obtained by recrystallization from methylene chloride. Data for **3b** were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV).[39] The structure was solved by Patterson methods and refined on F for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 4.

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Supporting Information Available: Details of the X-ray crystal structure determination of **3b**, including atomic positions, bond distances, bond angles, and torsional angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM021029+

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