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N-Heterocyclic Carbene Complexes of Nickel, Palladium, and Iridium Derived from Nitron: Synthesis, Structures, and Catalytic Properties

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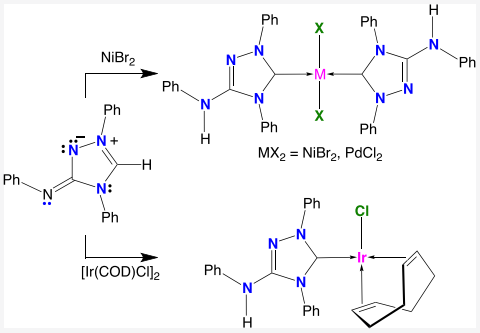
ABSTRACT: The mesoionic compound (1,4-diphenyl-1,2,4-triazol-4-ium-3-yl)-phenylazanide, commonly referred to as Nitron, has been employed as a "crypto-NHC" to afford 1,2,4-triazolylidene compounds of nickel, palladium, and iridium. Specifically, Nitron reacts with $NiBr_2$, $PdCl_2$, and $[Ir(COD)Cl]_2$ to afford the N-heterocyclic carbene complexes $(Nitron^{NHC})_2NiBr_2$, $(Nitron^{NHC})_2PdCl_2$, and $(Nitron^{NHC})Ir(COD)Cl$, respectively. The lattermost compound reacts with (i) CO to afford the dicarbonyl compound $(Nitron^{NHC})Ir(CO)_2Cl$ and (ii) CO, in the presence of PPh_3, to afford the monocarbonyl compound $(Nitron^{NHC})Ir(PPh_3)(CO)Cl$. Structural studies on $(Nitron^{NHC})Ir(COD)Cl$ and $(Nitron^{NHC})Ir(CO)_2Cl$ indicate that $Nitron^{NHC}$ has a stronger *trans* influence than does Cl; furthermore, IR spectroscopic studies on $(Nitron^{NHC})Ir(CO)_2Cl$ indicate that $Nitron^{NHC}$ is electronically similar to the structurally related Enders carbene but is less electron donating than imidazol-2-ylidenes with aryl substituents. Significantly, the $Nitron^{NHC}$ ligand affords catalytic systems, as illustrated by the ability of $(Nitron^{NHC})Ir(CO)_2Cl$ to effect (i) the dehydrogenation of formic acid, (ii) aldehyde hydrosilylation, (iii) dehydrocoupling of hydrosilanes and alcohols, and (iv) ketone reduction via transfer hydrogenation.



INTRODUCTION

So-called N-heterocyclic carbenes (NHCs) have emerged as an effective class of ligands in coordination chemistry with applications in catalysis.[1−4] A large variety of NHCs are currently available, many of which feature either one or two nitrogen atoms and owe their stability to donation of nitrogen lone pairs[5] to the divalent six-electron carbene[1,6] center (Figure 1). NHCs that incorporate three nitrogen atoms are also known, such that both 1,2,3-triazol-5-ylidenes[7] and 1,2,4-triazol-5-ylidenes[8] have likewise been the focus of considerable attention.[9] The first example of the latter class of molecules is provided by 1,3,4-triphenyl-1,2,4-triazol-5-ylidene, which is often referred to as Enders carbene (Figure 1). Conceptually related to Enders carbene is a derivative that features an exocyclic 4-NHPh rather than 4-Ph substituent (Figure 1); however, while this NHC has not been isolated, its long-known mesoionic tautomer, (1,4-diphenyl-1,2,4-triazol-4-ium-3-yl)-phenylazanide (Nitron),[10−14] exhibits reactivity that provides access to the carbene form (Figure 1).[15−19] For example, Nitron reacts with elemental sulfur to afford a thione derivative; likewise, Nitron has been used to obtain several metal complexes of the type $(Nitron^{NHC})ML_n$ (M = Ru, Rh, Cu, Ag, Au) that feature the 1,2,4-triazol-5-ylidene ligand, $Nitron^{NHC}$.[15−17] In view of this reactivity, Nitron has been referred to as a "crypto-NHC".[17,20] Here, we describe further applications of Nitron as a crypto-NHC to afford 1,2,4-triazolylidene compounds of nickel, palladium, and iridium, together with their structural and catalytic properties.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of $Nitron^{NHC}$ Complexes of Nickel and Palladium. Nitron reacts readily with $NiBr_2$ to afford the NHC complex $(Nitron^{NHC})_2NiBr_2$ (Scheme 1).[21] The formation of $(Nitron^{NHC})_2NiBr_2$ not only provides another example of how Nitron serves as a crypto-NHC but is also of note because of the high atom economy of the transformation. Specifically, while a variety of $(NHC)_2NiX_2$ complexes are known,[22−24] they are not usually synthesized via the direct reaction between an NHC and MX_2. For example, the first structurally reported nickel(II) NHC compounds, namely $(NHC)_2NiX_2$ (X = Cl, Br, I), were synthesized by (i) the reaction of the free NHC with $(Ph_3P)_2NiX_2$ and (ii) the *in situ* deprotonation of the azolium salt [H(NHC)]X by $Ni(OAc)_2$.[25,26] $(Ph_3P)_2NiX_2$ derivatives have subsequently been employed as reagents for the synthesis of many other $(NHC)_2NiX_2$ complexes by reaction with either the free NHC[27−29] or adducts, such as[NHC]LiBr,[28] [(NHC)-Ag]Br,[30−32] and $(NHC^{Me})SiCl_4$.[33] The reaction of $(Ph_3P)_2NiX_2$ with an amino acetal has also been reported to provide access to $(NHC)_2NiX_2$ derivatives.[34] In addition to the use of

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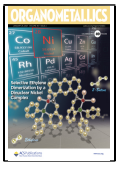

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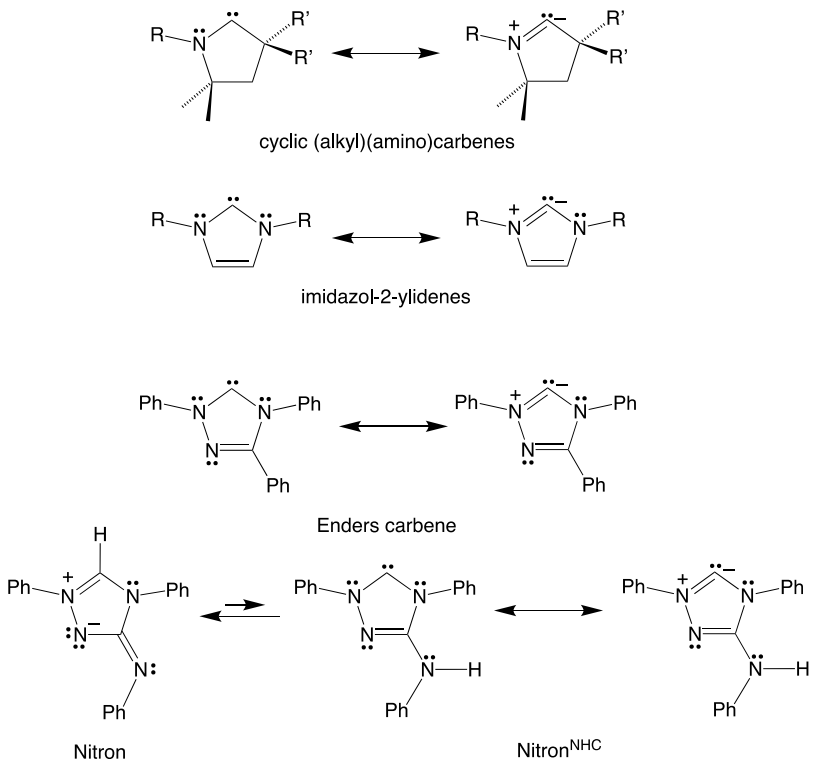
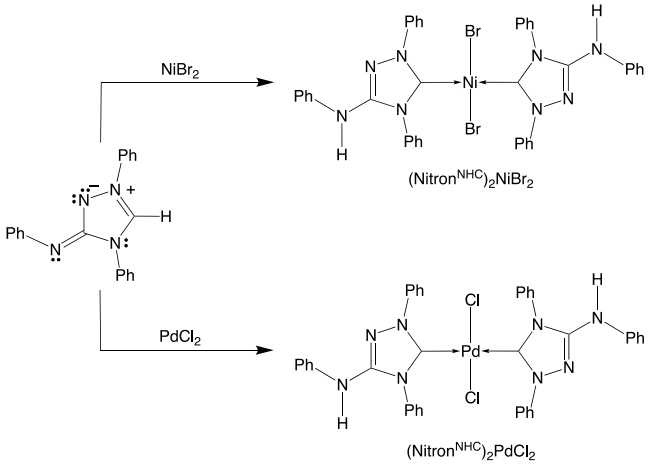


Figure 1. Examples of N-heterocyclic carbenes.

Scheme 1. Synthesis of (Nitron^{NHC})$_2$MX$_2$ from Nitron



$(Ph_3P)_2NiX_2$, other four-coordinate neutral adducts, such as $(py)_2NiCl_2$,[35] $NiX_2(DME)$,[36−38] $NiBr_2(THF)_2$,[38] and $NiBr_2(MeCN)_2$,[39] have likewise been used to synthesize $(NHC)_2NiX_2$ derivatives. The dicationic complex $[Ni(MeCN)_4](BF_4)_2$ has also been employed, but additional NaI is required to form $(NHC)_2NiI_2$ derivatives.[40] The second method described above, involving deprotonation of an azolium salt by $Ni(OAc)_2$, has similarly been adopted for the synthesis of a variety of $(NHC)_2NiX_2$ derivatives.[41−46] As an extension of this approach, other reactive nickel complexes, such as Cp_2Ni[47] and $(COD)_2Ni$,[48] and also indenyl[49] and fluorenyl[50] compounds have also been used to deprotonate azolium ions and thereby generate $(NHC)_2NiX_2$. By comparison to the two approaches indicated above, the formation of $(NHC)_2NiX_2$ by the method used here, i.e. the direct addition of the NHC (either isolated[51] or generated *in situ*[35,52,53]) to anhydrous NiX_2, has received relatively little attention in the literature.[54,55]

The molecular structure of (Nitron^{NHC})$_2$NiBr$_2$ has been determined by X-ray diffraction (Figure 2), which demonstrates that it is based on a square-planar geometry with mutually *trans* dispositions of both Nitron^{NHC} ligands and Br ligands. For example, the C−Ni−C and Br−Ni−Br bond angles are 180.0° and the four-coordinate τ_4 and τ_δ geometry indices are zero, both of which correspond to that for an idealized square-planar geometry.[56] However, despite these values, there is a scissoring distortion[57] such that the C−Ni−Br angles of 93.01(10) and 86.98(10)° deviate slightly from 90°. With respect to the square-planar nature of the structure, it is pertinent to note that, while this type of geometry is often observed for d^8 metal complexes,[58,59] d^8 nickel compounds are known to exhibit both square-planar and tetrahedral extremes.[60,61] The *trans* arrangement of the Nitron^{NHC} ligands in (Nitron^{NHC})$_2$NiBr$_2$ is in accord with the structures of most other $(NHC)_2NiX_2$ derivatives,[22] although structures with a *cis* disposition have

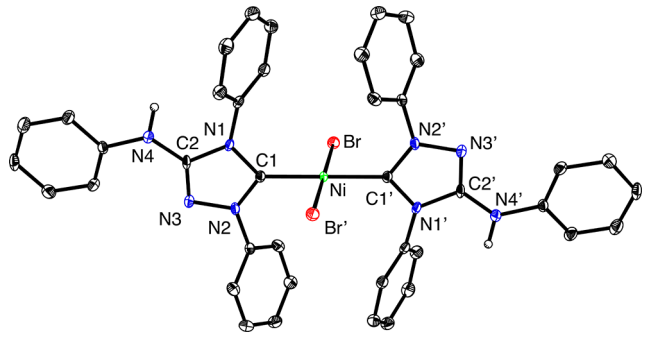


Figure 2. Molecular structure of (Nitron^{NHC})$_2$NiBr$_2$. Hydrogen atoms on carbon are omitted for clarity.

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also been observed, as illustrated by some chloride and isothiocyanate derivatives, $(NHC)_2NiCl_2$[31,33] and $(NHC)_2Ni(NCS)_2$.[62]

The Ni−C and Ni−Br bond lengths for $(Nitron^{NHC})_2NiBr_2$ are compared with other $(NHC)_2NiBr_2$ derivatives in Table 1, and the Ni−C bond length (1.894(3) Å) is comparable to the average value (1.900 Å) for structurally characterized $(NHC)_2NiX_2$ compounds listed in the Cambridge Structural Database (CSD).[63] For further comparison, the average Ni−C bond lengths in alkyl, aryl, and acetylide compounds are summarized in Table 2. Examination of these data indicate that there is a general decrease in Ni−C bond length as the s component of the sp^n hybrid increases, in accord with the well-known observation that C−X bond lengths decrease in the sequence $sp^3 > sp^2 > sp$.[64] In this regard, the Ni−C_{NHC} bond length (1.894(3) Å) is intermediate between the sp^2 Ni−Ar (1.961 Å) and sp Ni−C≡CR (1.875 Å) single-bond lengths but is distinctly longer than those in the few structurally characterized nickel compounds that have well-defined Ni=C double bonds which are devoid of heteroatom stabilization. For example, $(dtbpe)Ni{=}CPh_2$ is characterized by a Ni=C bond length of 1.836(2) Å,[65] while $(dtbpe)Ni{=}C(H)(C_6H_3Mes_2)$ possesses a bond length of 1.793(3) Å.[66,67]

The bonding in M−C_{NHC} moieties has been discussed in terms of both (i) π back-bonding[68] and (ii) the hybridization of the carbon, and the role of the latter has been emphasized for the late transition metals.[69] The participation of π back-bonding is very dependent on the system,[68] such that calculations on d^8 $(NHC)_2NiX_2$ compounds have characterized the Ni−C_{NHC} interactions as polar σ bonds.[31,70] In contrast to $(NHC)_2NiX_2$, π back-donation plays a much more significant role in the bonding of d^{10} $Ni(NHC)_2$ compounds,[71−73] which exhibit Ni−C_{NHC} bond lengths that are shorter than those of $(NHC)_2NiX_2$.

Similar to the reaction with $NiBr_2$, Nitron reacts with $PdCl_2$ to afford $(Nitron^{NHC})_2PdCl_2$ (Scheme 1), which also has a square-planar geometry (Figure 3) that exhibits a slight scissor distortion, as indicated by the C−Pd−Cl bond angles of 92.49(5) and 87.51(5)°. The Pd−C bond lengths (2.0138(15) Å) are comparable to the average Pd−C bond length for structurally characterized $(NHC)_2PdX_2$ compounds listed in the CSD (2.00 Å)[63] and are longer than the corresponding Ni−C bond lengths (1.894(3) Å) by a difference which is comparable to that predicted by the covalent radii of these elements (r_{Ni} = 1.24 Å and r_{Pd} = 1.39 Å).[64]

Table 1. Ni−C and Ni−Br Bond Lengths for $(NHC)_2NiBr_2$ Complexes

	d(Ni−C)/Å	d(Ni−Br)/Å	ref
$(Nitron^{NHC})_2NiBr_2$	1.894	2.327	this work
$(IPr^i)_2NiBr_2$	1.906	2.325	38
$(IPr^i)_2NiBr_2$	1.908, 1.918	2.291, 2.311	49
$(ICy)_2NiBr_2$	1.908	2.311	25
$(IMes^{Me})_2NiBr_2$	1.941	2.317	51
$(IPr)_2NiBr_2$	1.943, 1.943	2.296, 2.308	27a
$(BzIm^{Pm})_2NiBr_2$	1.893	2.300, 2.320	41
$(BzIm^{C3H5})_2NiBr_2$	1.900, 1.910	2.310	41
$(BzIm^{Bun})_2NiBr_2$	1.903	2.314	42
$(BzIm^{Bun})_2NiBr_2$	1.903	2.300	35
$(BzIm^{Pri})_2NiBr_2$	1.897	2.311	43
$(BzIm^{CH2Pri})_2NiBr_2$	1.913	2.300	43
$(BzIm^{CH2Ph})_2NiBr_2$	1.908	2.303	43
$(BzIm^{CHPh2})_2NiBr_2$	1.922	2.309	43

Table 2. Average M−C Bond Length Data[a] as a Function of Substituents on Carbon

bond type	hybridization	d(Ni−C)/Å	d(Pd−C)/Å	Δ(M−C)/Å[b]
M−CR_3	sp^3	2.010	2.083	0.073
M−CHR_2	sp^3	1.981	2.078	0.097
M−CH_2R	sp^3	1.960	2.046	0.086
M−CH_3	sp^3	1.960	2.050	0.090
M−Ar	sp^2	1.961	2.021	0.060
M−C_{NHC}	sp^2	1.900	2.000	0.100
M−C≡CR	sp	1.875	1.979	0.104

[a]Data taken from the CSD.[63] [b]Δ(M−C) = d(Pd−C) − d(Ni−C).

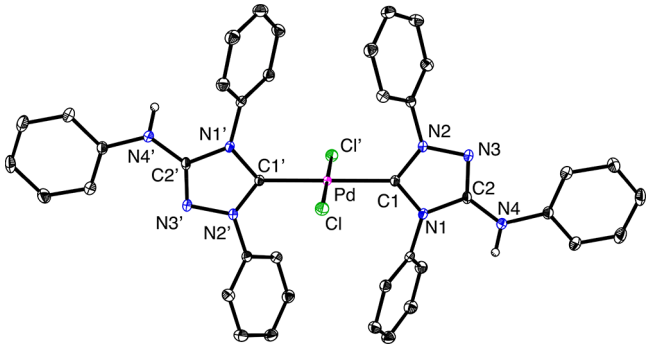

Figure 3. Molecular structure of $(Nitron^{NHC})_2PdCl_2$. Hydrogen atoms on carbon are omitted for clarity.

As noted above for nickel, the *trans* arrangement of the $Nitron^{NHC}$ ligands is consistent with the majority of $(NHC)_2PdX_2$ compounds, although the *cis* geometry is much more common for palladium. For example, whereas there are only 2 monodentate $(NHC)_2NiX_2$ compounds with a *cis* disposition listed in the CSD,[63,74] there are 45 such palladium derivatives.[75] In some cases, the palladium $(NHC)_2PdX_2$ compounds have been isolated as both *cis* and *trans* isomers.[76−90] For many of these examples, the *cis* isomer has been identified as the more stable isomer,[79−87] whereas in others the *trans* form has been either experimentally[88,89] or computationally[90] identified as the more stable isomer.[91] In view of these observations pertaining to the existence of both *cis* and *trans* $(NHC)_2MX_2$ isomers, including examples where there are phenyl substituents on nitrogen,[80] we considered it pertinent to evaluate this possibility for $(Nitron^{NHC})_2NiBr_2$ and $(Nitron^{NHC})_2PdCl_2$ by using computational methods.

The molecular structures of various isomeric forms of $(Nitron^{NHC})_2NiBr_2$ and $(Nitron^{NHC})_2PdCl_2$ were, therefore, determined by density functional theory (DFT) geometry optimization procedures, as illustrated in Figures 4 and 5. Both *syn* and *anti* rotamers were evaluated, and in each case, the *trans* isomers are lower in energy than the *cis* isomers, which is in accord with the experimentally observed structures.[92] It is also worth noting that, by comparison to the *trans* isomers, the *cis* complexes are distorted from a square-planar geometry to a greater degree, as indicated by the magnitude of the deviation of the four-coordinate τ_4 and τ_6 geometry indices from zero (Table 3).

Synthesis and Structural Characterization of $Nitron^{NHC}$ Complexes of Iridium. In addition to nickel and palladium, Nitron can also be employed to obtain an NHC iridium complex.[93] Specifically, Nitron reacts with

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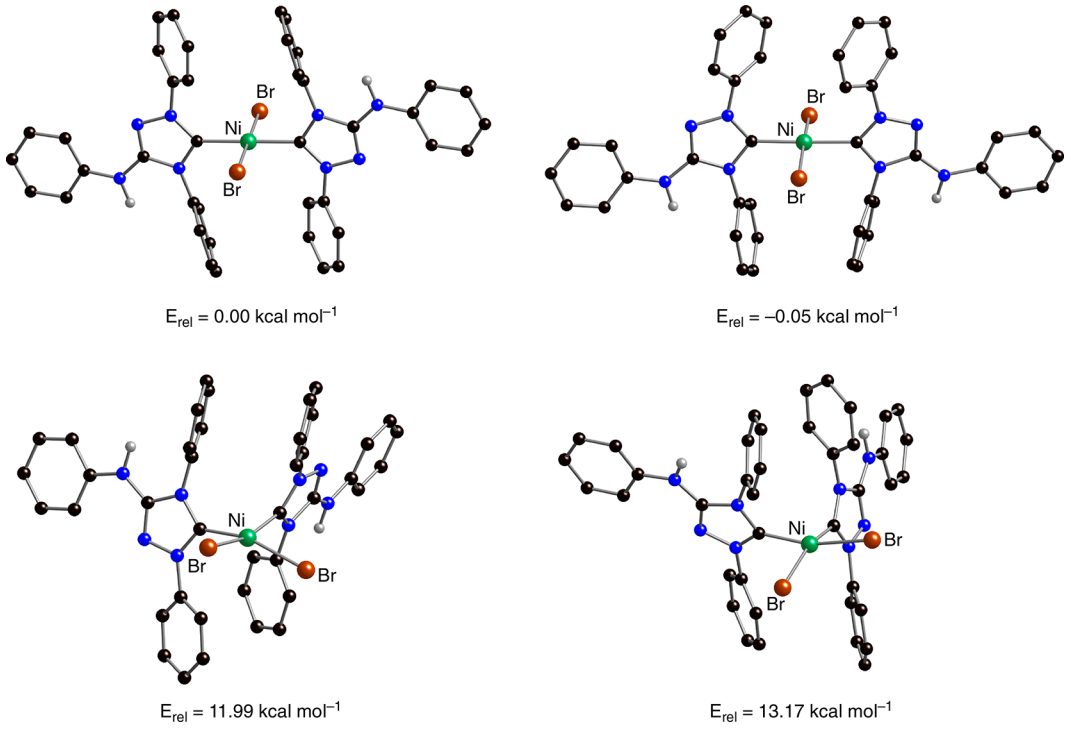

Figure 4. Geometry-optimized structures of isomers of $(Nitron^{NHC})_2NiBr_2$.

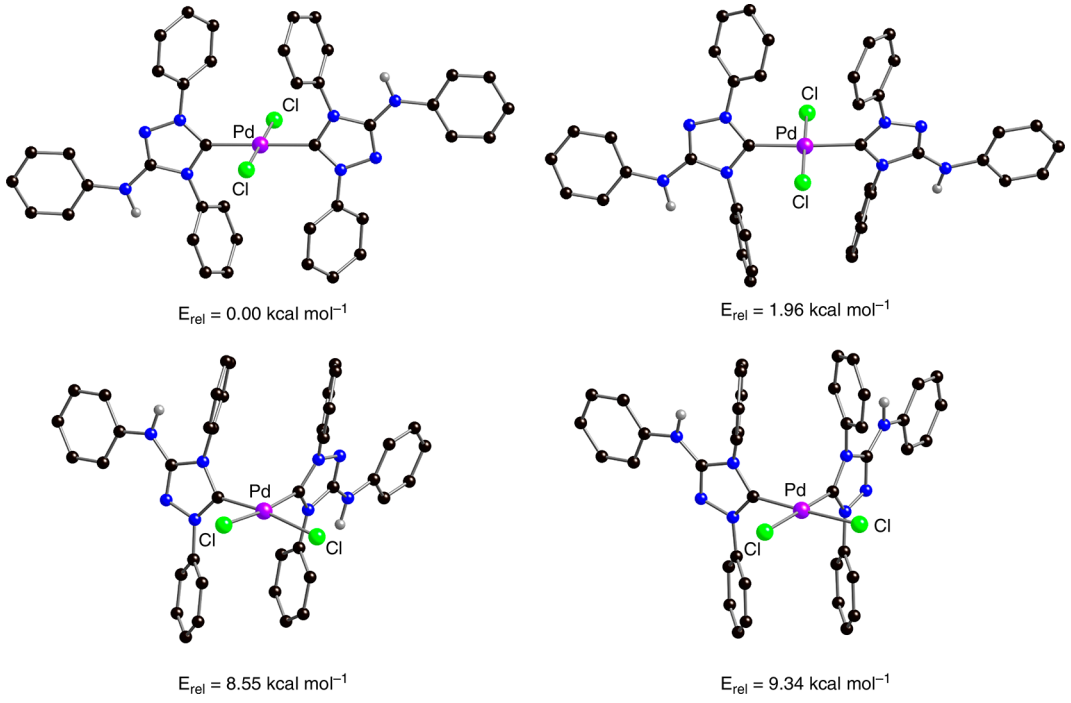

Figure 5. Geometry-optimized structures of isomers of $(Nitron^{NHC})_2PdCl_2$.

Table 3. Four-Coordinate Indices[56] for Geometry-Optimized $(Nitron^{NHC})_2MX_2$

	τ_4, τ_6	
isomer	$(Nitron^{NHC})_2NiBr_2$	$(Nitron^{NHC})_2PdCl_2$
trans, anti	0.00, 0.00	0.00, 0.00
trans, syn	0.08, 0.08	0.06, 0.05
cis, anti	0.28, 0.28	0.01, 0.01
cis, syn	0.26, 0.26	0.12, 0.12

$[Ir(COD)Cl]_2$ to afford $(Nitron^{NHC})Ir(COD)Cl$, as illustrated in Scheme 2.[94]

The molecular structure of $(Nitron^{NHC})Ir(COD)Cl$ has been determined by X-ray diffraction (Figure 6), and the Ir−C_{NHC} bond length of 2.014(4) Å compares favorably with those of other (NHC)Ir(COD)Cl derivatives listed in the CSD, for which the average is 2.035 Å, with some examples being presented in Table 4.[95−105]

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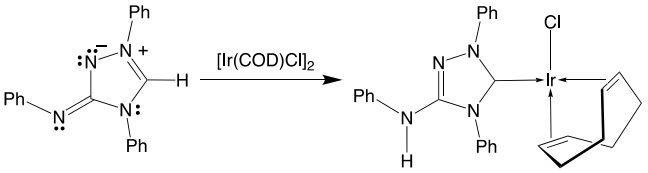
Scheme 2. Synthesis of (Nitron^{NHC})Ir(COD)Cl



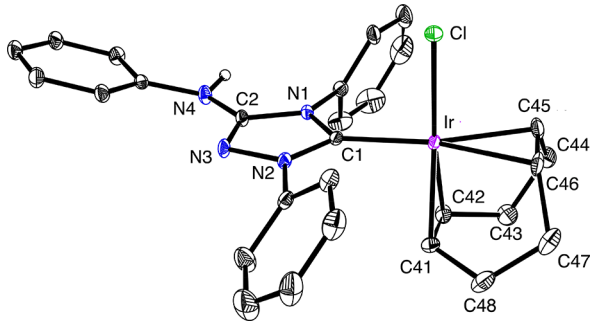


Figure 6. Molecular structure of (Nitron^{NHC})Ir(COD)Cl. Hydrogen atoms on carbon and hydrogen-bonded acetonitrile are omitted for clarity.

Table 4. Ir−C_{NHC} Bond Lengths in (NHC)Ir(COD)Cl Compounds

	d(Ir−C_{NHC})/Å	ref
(Nitron^{NHC})Ir(COD)Cl	2.014	this work
(ICy)Ir(COD)Cl	2.091	95
(IBu^t)Ir(COD)Cl	2.056, 2.074	95
(IBu^t)Ir(COD)Cl	2.063, 2.069	97
(IAd)Ir(COD)Cl	2.058, 2.061, 2.064, 2.073	95
(ICH_2Tol)Ir(COD)Cl	2.028	98
(IPr)Ir(COD)Cl	2.054, 2.055	95
(IMes)Ir(COD)Cl	2.048, 2.055	95
(IPh,Me)Ir(COD)Cl	2.028, 2.029	99
(IMesBr)Ir(COD)Cl	2.041	100
(IMesBr)Ir(COD)Cl	2.042	101
(IPrBr)Ir(COD)Cl	2.035	101
(SIPr)Ir(COD)Cl	2.041, 2.049	95
(SIMes)Ir(COD)Cl	2.041	95
(IPr^{OMe})Ir(COD)Cl	2.039	102
(SIPr^{OMe})Ir(COD)Cl	2.020	102
(IPr*)Ir(COD)Cl	2.056	102
(IPr*^{OMe})Ir(COD)Cl	2.063	102
(2-SICyNap)Ir(COD)Cl	2.034	103
(2,7-SICyNap)Ir(COD)Cl	2.052	103
(BzIm^{Pri})Ir(COD)Cl	2.020	104
(Bz^{Me}Im^{Pri})Ir(COD)Cl	2.028	104

The Ir−C bonds associated with the olefin moiety are longer than that of the Ir−C_{NHC} bond, with those *trans* to the Nitron^{NHC} ligand (2.162(5) and 2.182(5) Å) being longer than those *cis* to Nitron^{NHC} (i.e. *trans* to Cl) (2.092(5) and 2.109(5) Å); as such, it is evident that the Nitron^{NHC} ligand exerts a stronger *trans* influence than does Cl.[98,104,106,107] These differences in Ir−C bond lengths are reproduced in the DFT geometry optimized structure (Figure 7): namely, Ir−C_{NHC} (2.027 Å), Ir−C_{trans} (2.217 and 2.249 Å), and Ir−C_{cis} (2.127 and 2.147 Å). One other noteworthy structural feature of (Nitron^{NHC})Ir(COD)Cl is that the N−H group participates in a hydrogen-bonding interaction with a molecule of acetonitrile,

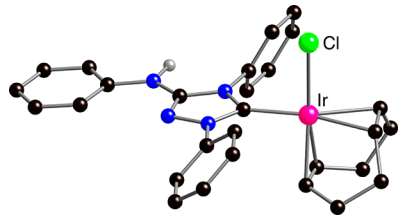


Figure 7. DFT geometry optimized structure of (Nitron^{NHC})Ir(COD)-Cl.

with an N···N distance of 3.017(7) Å, which is slightly shorter than the average value of 3.11 Å for compounds with N−H···NCMe interactions listed in the CSD.[108]

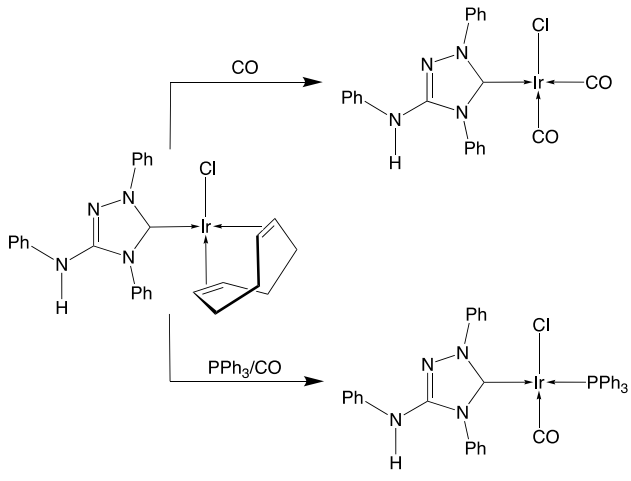
(Nitron^{NHC})Ir(COD)Cl provides access to other Nitron^{NHC} iridium complexes. For example, (Nitron^{NHC})Ir(COD)Cl reacts with CO to afford the dicarbonyl (Nitron^{NHC})Ir$(CO)_2$Cl,[94] while the mixed triphenylphosphine/carbonyl derivative (Nitron^{NHC})Ir(PPh_3)(CO)Cl is obtained from the reaction of (Nitron^{NHC})Ir(COD)Cl with PPh_3 in the presence of CO (Scheme 3).

The molecular structures of (Nitron^{NHC})Ir$(CO)_2$Cl (Figure 8) and (Nitron^{NHC})Ir(PPh_3)(CO)Cl (Figure 9) have been determined by X-ray diffraction, which demonstrates that both compounds have a common square-planar geometry. For example, the τ_4 and τ_δ geometry indices[57] of (Nitron^{NHC})Ir-$(CO)_2$Cl are 0.04, while those for (Nitron^{NHC})Ir$(CO)(PPh_3)$Cl are 0.07. In contrast to dicarbonyl derivatives (NHC)Ir-$(CO)_2$Cl,[109−114] structurally characterized monocarbonyl compounds (NHC)Ir(PPh_3)(CO)Cl are not common, with only (ICH_2Ph)Ir(PPh_3)(CO)Cl and $(SICH_2Ph)$Ir(PPh_3)(CO)Cl having been reported.[115,116] In each of these compounds the PPh_3 ligand is *trans* to the NHC ligand.

The Ir−C_{NHC} bonds of (Nitron^{NHC})Ir$(CO)_2$Cl and (Nitron^{NHC})Ir(PPh_3)(CO)Cl are distinctly longer than the Ir−CO bonds. For example, the Ir−C_{NHC} bond length of (Nitron^{NHC})Ir$(CO)_2$Cl is 2.064(2) Å, while the *cis* and *trans* Ir−CO bond lengths are 1.844(3) and 1.892(3) Å, respectively. This difference is in accord with the notion that, by comparison to NHC ligands, CO is a very effective π acceptor,[121] thereby resulting in shorter Ir−CO bonds.

With respect to the dicarbonyl compound (Nitron^{NHC})Ir-$(CO)_2$Cl, the Ir−CO bond that is *trans* to the Nitron^{NHC} ligand

Scheme 3. Synthesis of (Nitron^{NHC})Ir$(CO)_2$Cl and (Nitron^{NHC})Ir(PPh_3)(CO)Cl



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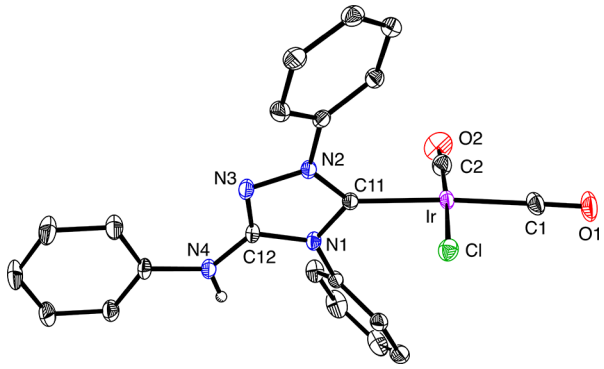

Figure 8. Molecular structure of (Nitron^{NHC})Ir(CO)$_2$Cl. Hydrogen atoms on carbon are omitted for clarity.

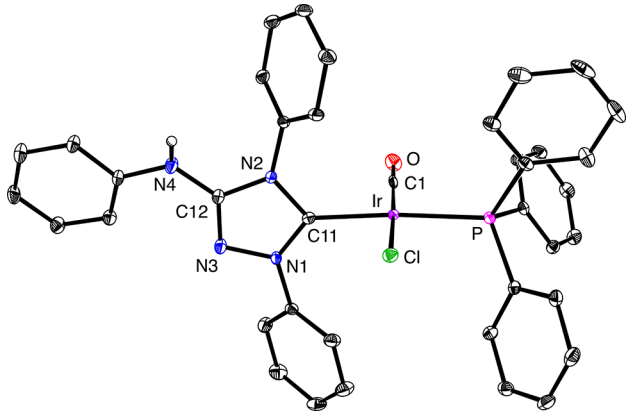

Figure 9. Molecular structure of (Nitron^{NHC})Ir(PPh$_3$)(CO)Cl. Hydrogen atoms on carbon are omitted for clarity.

is longer than that *trans* to the Cl ligand, which is again in accord with Nitron^{NHC} having a stronger *trans* influence than Cl, as noted above for (Nitron^{NHC})Ir(COD)Cl. These differences in Ir−C bond lengths are also reproduced in the DFT geometry optimized structure (Figure 10): namely, Ir−C$_{NHC}$ (2.087 Å), Ir−C$_{trans}$ (1.905 Å), and Ir−C$_{cis}$ (1.847 Å).

A consideration of other dicarbonyl complexes indicates that Ir−C$_{NHC}$ bonds of (NHC)Ir(CO)$_2$Cl derivatives are also longer than the Ir−CO bonds (Table 5). Although for most of these compounds the Ir−CO bond that is *trans* to the NHC ligand is also longer than the *cis* bond, there are some examples where the opposite trend has been reported (Table 5). While the occurrence of these different trends in bond length could possibly be interpreted as indicating different trans influence abilities of NHC ligands in (NHC)Ir(CO)$_2$Cl complexes, prior to doing so it is important to consider the impact of unresolved disorder between pairs of mutually *trans* CO and Cl ligands.

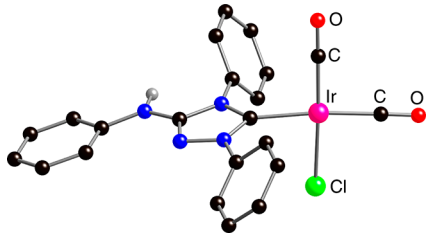

Figure 10. DFT geometry optimized structure of (Nitron^{NHC})Ir(CO)$_2$Cl. Hydrogen atoms on carbon are omitted for clarity.

Specifically, square-planar ML$_2$(CO)X compounds may exhibit disorder between pairs of mutually *trans* CO and X ligands[117] and this type of disorder can result in an artificial apparent lengthening of the Ir−CO bond that is *cis* to the NHC ligand.[106,118,119] An illustration of the ability of disorder to influence the Ir−CO bond lengths in this system is provided by the fact that there are several derivatives that possess more than one crystallographically independent molecule in the asymmetric unit and, for these structures, the Ir−CO bond lengths for the ligands that are *trans* to Cl are significantly different. For example, the Ir−CO bond lengths for the carbonyl groups that are *cis* to the NHC ligand in the two crystallographically independent molecules of (SIPr)Ir(CO)$_2$Cl differ considerably, namely 1.855(6) and 1.959(4) Å, whereas those that are *trans* to the NHC ligand are much more similar, namely 1.872(5) and 1.883(5) Å.[95] Further evidence that the 1.959(4) Å bond is artificially lengthened is provided by the fact that the equivalent isotropic displacement parameter (U_{eq}) for the *cis*-carbonyl carbon atom is very small (0.0041 Å^2); for comparison, U_{eq} values for the other carbonyl carbon atoms range from 0.0322 to 0.0353 Å^2. The small value of U_{eq} is likely a consequence of the presence of chlorine, which results in the site possessing more electron density than that associated with a carbon atom. As another illustration of the impact of unresolved disorder, the Ir−CO bond *trans* to Cl in (2,7-SICyNap)Ir(CO)$_2$Cl (1.995(3) Å) is also considerably longer than that *trans* to the NHC ligand (1.898(3) Å), and U_{eq} for the carbonyl carbon is also smaller (0.0192 versus 0.0263 Å^2).[103] In contrast to the dicarbonyls (NHC)Ir(CO)$_2$Cl, the cyclooctadiene complexes (NHC)Ir(COD)Cl are not subject to a similar type of disorder; as such, structural studies on these compounds may provide a more reliable approach for evaluating the relative *trans* influences of NHC ligands.

The dicarbonyl complex (Nitron^{NHC})Ir(CO)$_2$Cl is also of relevance because the LIr(CO)$_2$Cl platform has been introduced as a convenient alternative to LNi(CO)$_3$[120] for evaluating the electron-donating properties of a donor ligand.[2b,95,98,102−114,121−126] Specifically, the Tolman electronic parameter (TEP), which is the frequency of the A$_1$ symmetry ν(CO) vibrational mode of LNi(CO)$_3$ complexes and is an indicator of the donor ability of the L ligand,[127,128] is empirically related to the average value of the ν(CO) stretching frequencies (in cm^{-1}) of LIr(CO)$_2$Cl via the expression TEP = 0.8475[ν-(CO)$_{av}$] + 336.2.[2b,95,129] On this basis, the value of ν(CO)$_{av}$ for (Nitron^{NHC})Ir(CO)$_2$Cl (2030.0 cm^{-1}) predicts a TEP of 2056.6 cm^{-1} for Nitron^{NHC}, which compares favorably to the value of 2057.4 cm^{-1} predicted by using the rhodium counterpart[15] and the corresponding empirical relationship for the rhodium system LRh(CO)$_2$Cl.[130] Both the ν(CO)$_{av}$ values for (Nitron^{NHC})Ir(CO)$_2$Cl and the TEP value indicate that the electronic properties of Nitron^{NHC} are very similar to those of the structurally similar Enders carbene (2030.8 and 2057.3 cm^{-1}, respectively).[95,121] However, it is evident that Nitron^{NHC} is less electron donating than imidazol-2-ylidenes with aryl substituents. For example, (IMes)Ir(CO)$_2$Cl is characterized by ν(CO)$_{av}$ and TEP values of 2023 and 2051 cm^{-1}, respectively.[121,123]

While the steric properties of ligands have traditionally been expressed in terms of the Tolman cone angle and related concepts,[131] the steric properties of NHC ligands are generally expressed in terms of the so-called "buried volume" (%V_{bur}), which corresponds to the portion of the volume of a sphere centered on the metal atom that is buried by overlap with the

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Table 5. Ir−C Bond Length Data for $(NHC)_2Ir(CO)_2Cl$

	d(Ir−C_{NHC})/Å	d(Ir−CO_{cis})[a]/Å	d(Ir−CO_{trans})[a]/Å	ref
(Nitron^{NHC})Ir(CO)$_2$Cl	2.064	1.843	1.892	this work
(Nitron^{NHC})Ir(PPh_3)(CO)Cl	2.047(3)	1.850(4)		this work
(IPr^i)Ir(CO)$_2$Cl[b]	2.069	1.840	1.881	109
(IBu^t)Ir(CO)$_2$Cl	2.115	1.813	1.873	95
(IAd)Ir(CO)$_2$Cl	2.103, 2.098	1.869, 1.882	1.959, 1.954	95
(ICy)Ir(CO)$_2$Cl	2.078, 2.052	1.611, 1.749	1.847, 1.861	95
(IPr)Ir(CO)$_2$Cl	2.079	1.857	1.886	95
(SIPr)Ir(CO)$_2$Cl	2.082, 2.071	1.855, 1.959	1.872, 1.883	95
(SIEt)Ir(CO)$_2$Cl	2.110	1.766	1.883	116
(IMes)Ir(CO)$_2$Cl	2.058, 2.068, 2.078, 2.108	1.833, 1.856, 1.842, 1.654	1.904, 1.876, 1.937, 1.860	95
(SIMes)Ir(CO)$_2$Cl	2.122	1.720	1.915	95
(ICy^8)Ir(CO)$_2$Cl	2.097	1.851	1.895	110
(ICy^{12})Ir(CO)$_2$Cl	2.081	1.986	1.899	110
(C_sIMes)Ir(CO)$_2$Cl	2.096	1.828	1.890	114
(C_sIMes)Ir(CO)$_2$Cl	2.079	1.859	1.887	114
(IBiox6)Ir(CO)$_2$Cl	2.072	1.897	1.892	113
(2,7-SICyNap)Ir(CO)$_2$Cl	2.079	1.995	1.898	103
(BIANIPr)Ir(CO)$_2$Cl	2.090	1.850	1.850	106
(IMes,Me)Ir(CO)$_2$Cl	2.093, 2.104	1.836, 1.790	1.898, 1.891	99
(2-SIMorNap)Ir(CO)$_2$Cl	2.077	1.936	1.897	106
(2-SIPipNap)Ir(CO)$_2$Cl	2.094	1.792	1.912	106
(IMes-C_7)Ir(CO)$_2$Cl	2.076, 2.120	1.883, 1.856	1.889, 1.925	111

[a]*cis* and *trans* refer to positions relative to the NHC ligand. [b]There are two crystallographically independent molecules, one of which is recognized to exhibit CO/Cl disorder. Data are only given for the ordered molecule.

ligand atoms.[132−134] The %V_{bur} value for Nitron^{NHC} in (Nitron^{NHC})Ir(CO)$_2$Cl using coordinates from the X-ray structure determination is 32.2%, but for comparison with other systems, we have also evaluated %V_{bur} for a structure in which the Ir−L bond is fixed at 2.10 Å;[132d] these data indicate that Nitron^{NHC} has similar steric properties to those of related NHC ligands with aryl substituents (Table 6). In addition to describing the overall steric bulk via the value of %V_{bur}, finer details of the ligand profile are afforded by examination of steric maps[102,135] that illustrate how the steric bulk is distributed about the metal center via the use of colored contours, and the steric map for (Nitron^{NHC})Ir is illustrated in Figure 11.

Catalytic Reactivity of Nitron^{NHC} Iridium Complexes. We are currently interested in developing catalytic applications of metal complexes with respect to transformations that involve C−O bonds. As an illustration, we have previously described catalysts for the (i) decarboxylation of formic acid to release H_2,[136] a reaction that is of interest regarding the use of formic acid as a medium for storing hydrogen with respect to energy

Table 6. %V_{bur} Values for NHC as Determined for $(NHC)Ir(CO)_2Cl$ with an Ir−NHC Distance of 2.10 Å

NHC	%V_{bur}	ref
Nitron^{NHC}	31.6	this work
IPh	30.5	132d
SIPh	31.6	132d
ITol	30.5	132d
SITol	32.4	132d
IMes	31.6	132d
SIMes	32.7	132d
IPr	33.6	132d
SIPr	35.7	132d
IBu^t	35.5	132d
IAd	36.1	132d

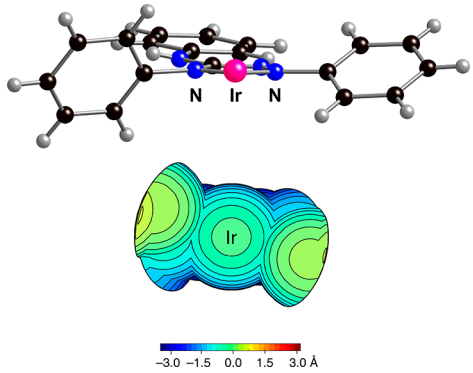

Figure 11. Steric map for the Nitron^{NHC} ligand of (Nitron^{NHC})Ir(CO)$_2$Cl. The view of the [(Nitron^{NHC})Ir] moiety is along the Ir−C bond, such that the NHC carbon atom is obscured by the iridium. The iridium is located at a distance of 2.10 Å in front of the NHC carbon atom (which is obscured in this view), and the CO and Cl ligands are not included in the calculation.

applications,[137,138] and (ii) hydrosilylation of carbonyl compounds, including the conversion of CO_2 to silyl formates and bis(silyl)acetals.[139−141] Since NHC ligands have found widespread use in catalysis,[142] we sought to develop catalytic applicatons of Nitron^{NHC} metal complexes. Therefore, it is of note that (Nitron^{NHC})Ir(CO)$_2$Cl provides a catalyst for the dehydrogenation of formic acid (Scheme 4) at 80 °C.[143−145]

In addition, (Nitron^{NHC})Ir(CO)$_2$Cl is also a catalyst for the hydrosilylation of carbonyl compounds to afford alkoxysilanes, a transformation that is not only of interest in terms of providing a means to reduce a substrate to an alcohol[146] but is also of

Scheme 4. Dehydrogenation of Formic Acid

$$HCO_2H \xrightarrow{[Ir]} CO_2 + H_2$$

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interest because alkoxysilanes have applications in organic synthesis[147] and materials chemistry.[148] For example, (Nitron^{NHC})Ir(CO)$_2$Cl effects the insertion of PhCHO into two of the Si−H bonds of $PhSiH_3$ at 60 °C to afford the alkoxysilane $PhSiH(OCH_2Ph)_2$ with a TOF of 23 h^{-1} [149] and one of the Si−H bonds of Ph_2SiH_2 at 60 °C to afford $Ph_2Si(OCH_2Ph)H$ with a TOF of 8 h^{-1} (Scheme 5).[150]

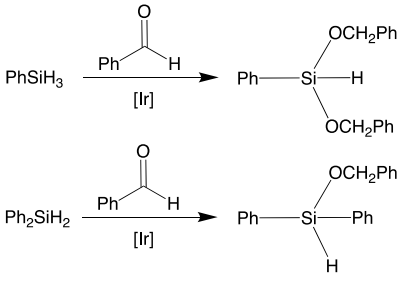
Alkoxysilanes can also be obtained by the catalytic dehydrocoupling of $PhSiH_3$ and alcohols, a class of reaction that is of interest because it releases H_2 on demand and is thereby of relevance to the "hydrogen economy".[151,152] For example, (Nitron^{NHC})Ir(CO)$_2$Cl serves as a catalyst for the rapid formation of a 1.5:1 mixture of $PhSiH(OCH_2Ph)_2$ and $PhSi(OCH_2Ph)_3$ via the room-temperature dehydrocoupling of $PhSiH_3$ and $PhCH_2OH$, with TOF > 320 h^{-1} per Si−H bond, followed by the complete conversion to $PhSi(OCH_2Ph)_3$ over a period of 1 day (Scheme 6). Dehydrocoupling of Ph_2SiH_2 with $PhCH_2OH$ immediately affords the mono-alkoxide $Ph_2SiH(OCH_2Ph)$, while conversion to the bis-alkoxide $Ph_2Si(OCH_2Ph)_2$ occurs over a period of several days at room temperature.

The dehydrocoupling of $PhSiH_3$ and MeOH is much more efficient and immediately generates a mixture of $PhSiH(OMe)_2$ and $PhSi(OMe)_3$, which converts more slowly to $PhSi(OMe)_3$; the initial TOF is 195000 h^{-1}. Likewise, dehydrocoupling between Ph_2SiH_2 and MeOH immediately gives $Ph_2SiH(OMe)$, which converts more slowly to $Ph_2Si(OMe)_2$; the initial TOF is 6500 h^{-1}.

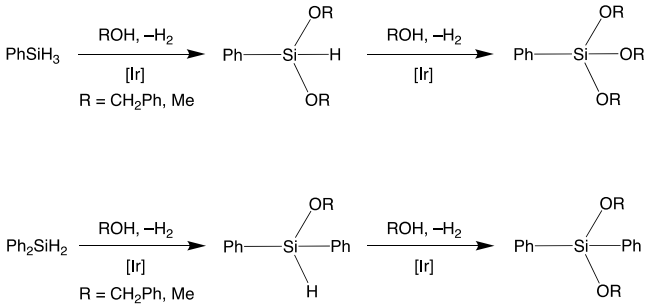
Finally, in the presence of base, (Nitron^{NHC})Ir(CO)$_2$Cl also provides a catalytic system for transfer hydrogenation,[153−155] as illustrated by the reduction of PhC(O)Me to PhCH(OH)Me by Pr^{i}OH (Scheme 7). More interestingly, (Nitron^{NHC})Ir(CO)$_2$Cl is also capable of achieving catalytic transfer hydrogenation using methanol, which has been much less utilized for transfer hydrogenation[156,157] than has Pr^{i}OH.[153] Such transformations, however, are of relevance to the use of methanol as a liquid organic hydrogen carrier[138,158] and the methanol economy.[159] Therefore, it is significant that methanol likewise reduces PhC(O)Me to PhCH(OH)Me in the presence of (Nitron^{NHC})Ir(CO)$_2$Cl and base. Interestingly, in addition to PhCH(OH)Me, small quantities of PhC(O)Et (8:1) are also formed due to a so-called hydrogen-borrowing pathway.[160]

The ability of (Nitron^{NHC})Ir(CO)$_2$Cl to afford catalytic systems has precedent with the use of other NHC-iridium compounds that have been employed for the dehydrogenation of formic acid,[144] the hydrosilylation of benzaldehyde,[161] the transfer hydrogenation of ketones,[162] and the dehydrocoupling of hydrosilanes and alcohols.[152a,b] With respect to the latter, the high TOF for the reactions of $PhSiH_3$ and Ph_2SiH_2 with MeOH compare favorably with those reported for other iridium compounds;[152a,b] for example, Cp*Ir(NHC)Cl$_2$ (0.5%) releases 3.0 equiv of H_2 from $PhSiH_3$ over a period of 5 min, while Ph_2SiH_2 releases 1.6 equiv of H_2 over a period of 2 h.[152a]

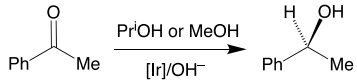
Scheme 5. Hydrosilylation of Benzaldehyde



Scheme 6. Dehydrocoupling of Hydrosilanes and Alcohols



Scheme 7. Transfer Hydrogenation of Acetophenone



CONCLUSIONS

In summary, we have employed the mesoionic compound Nitron as a "crypto-NHC" to afford 1,2,4-triazolylidene compounds of nickel, palladium, and iridium. Specifically, Nitron reacts with $NiBr_2$, $PdCl_2$, and $[Ir(COD)Cl]_2$ to afford (Nitron^{NHC})$_2$NiBr$_2$, (Nitron^{NHC})$_2$PdCl$_2$, and (Nitron^{NHC})Ir(COD)Cl, respectively. The latter compound has been used to obtain other Nitron^{NHC} iridium(I) derivatives: namely, the carbonyl complexes (Nitron^{NHC})Ir(CO)$_2$Cl and (Nitron^{NHC})Ir(PPh_3)(CO)Cl. Structural studies on (Nitron^{NHC})Ir(COD)Cl and (Nitron^{NHC})Ir(CO)$_2$Cl indicate that Nitron^{NHC} has a stronger *trans* influence than Cl. Furthermore, IR spectroscopic studies on (Nitron^{NHC})Ir(CO)$_2$Cl indicate that while Nitron^{NHC} possesses electronic properties that are comparable to those of the structurally similar Enders carbene, it is less electron donating than imidazol-2-ylidenes with aryl substituents. Evaluation of the so-called "buried volume" indicates that Nitron^{NHC} has steric properties similar to those of related NHC ligands with aryl substituents. Finally, we have demonstrated that the Nitron^{NHC} ligand affords catalytic systems, as illustrated by the ability of (Nitron^{NHC})Ir(CO)$_2$Cl to effect (i) dehydrogenation of formic acid, (ii) hydrosilyation of benzaldehyde, (iii) dehydrocoupling of hydrosilanes and alcohols, and (iv) reduction of acetophenone *via* transfer hydrogenation.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under an argon or nitrogen atmosphere unless otherwise specified.[163] Solvents were purified and degassed by using standard procedures. ^{1}H NMR spectra were measured on Bruker AVIII 300, Bruker AVIII 400, and Bruker AVIII 500 spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ (δ 0) and were referenced internally with respect to the protio solvent impurity (δ 128.06 for C_6D_6 and δ 118.26 for CD_3CN).[164] ^{31}P{^{1}H} NMR spectra are reported in ppm relative to 85% H_3PO_4 (δ 0) and were obtained by using the Ξ/100% value of 40.480742.[165] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ (δ 0) and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6).[164] Coupling constants are given in hertz. Infrared spectra were recorded on a PerkinElmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode and are reported in

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reciprocal centimeters. Accurate mass (HRMS) measurements were performed on a Waters Xevo G2-XS QTOF mass spectrometer equipped with a LockSpray source and Atmospheric pressure Solids Analysis Probe (ASAP). The solid sample was swabbed with the probe, which was then inserted into the source with a source gas (nitrogen) temperature of 600 °C. The probe remained in the source for 1 min or until sample peaks were no longer observed, after which the probe was removed. The APCI+ corona pin current was set to 0.8 μA. The calculation of the percent buried volumes (%V_{bur}) and the steric maps was determined by using SambVca 2.0 (https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html; retrieved July 26, 2020),[132a] for a sphere of radius 3.5 Å about the metal center and Bondi van der Waals radii scaled by a factor of 1.17.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[166] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2038698−2038702).

Computational Details. Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[167] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets, and Cartesian coordinates are provided in the Supporting Information.

Synthesis of (Nitron^{NHC})Ir(COD)Cl. A suspension of [Ir(COD)Cl]$_2$ (245 mg, 365 mmol) in acetonitrile (10 mL) was treated with Nitron (228 mg, 730 mmol) and stirred for 21 h, resulting in the formation of a yellow precipitate in a dark brown solution. The precipitate was isolated *via* centrifugation, washed with diethyl ether (1 × 2 mL), and dried *in vacuo* to afford (Nitron^{NHC})Ir(COD)Cl as a yellow powder (302 mg, 64%). Yellow crystals suitable for X-ray diffraction were obtained *via* slow evaporation of an acetonitrile solution. ^{1}H NMR (C_6D_6): 1.25 [m, 1H of COD], 1.45 [m, 4H of COD], 1.63 [m, 1H of COD], 1.90 [m, 1H of COD], 2.04 [m, 1H of COD], 2.45 [m, 1H of COD], 2.84 [m, 1H of COD], 4.97 [m, 1H of COD], 5.05 [m, 1H of COD], 5.82 [s, 1H of Nitron^{NHC} N−H], 6.84 [t, 1H of Nitron^{NHC}, $^3J_{H-H}$ = 7 Hz], 7.09 [m, 6H of Nitron^{NHC}], 7.17 [t, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz], 7.24 [t, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz], 7.63 [br, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz], 8.93 [d, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz]. ^{13}C{^{1}H} NMR (C_6D_6): 29.2 [s, *C*H$_2$ of COD], 30.3 [s, *C*H$_2$ of COD], 32.7 [s, *C*H$_2$ of COD], 34.3 [s, *C*H$_2$ of COD], 52.2 [s, *C*H of COD]. 52.8 [s, *C*H of COD], 84.5 [s, *C*H of COD], 86.2 [s, *C*H of COD], 118.0 [Nitron^{NHC}], 123.0 [Nitron^{NHC}], 123.8 [Nitron^{NHC}], 128.9 [Nitron^{NHC}], 129.2 [Nitron^{NHC}], 129.5 [Nitron^{NHC}], 129.9 [Nitron^{NHC}], 134.8 [Nitron^{NHC}], 138.6 [Nitron^{NHC}], 140.5 [Nitron^{NHC}], 149.7 [Nitron^{NHC}], 182.3 [s, *C*N$_2$ of Nitron^{NHC}]. Anal. Calcd for (Nitron^{NHC})Ir(COD)Cl: C, 51.9; H, 4.4; N, 8.6. Found: C, 52.3; H, 4.1; N, 8.4. IR (cm^{-1}): 3289 (w), 2882 (w), 2833 (w), 1630 (m), 1596 (m), 1489 (m), 1452 (w), 1369 (m), 1320 (w), 1233 (w), 1170 (w), 971 (m), 751 (s), 693 (s), 506 (m).

Synthesis of (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(COD)Cl (20 mg, 0.031 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was degassed *via* a freeze−pump−thaw cycle and then exposed to CO (1 atm). The solution immediately turned a paler yellow color and was occasionally shaken for 1 h. The volatile components were then removed *via* lyophilization to afford a pale yellow powder, which was washed with pentane (1 × 2 mL) and dried *in vacuo* to afford (Nitron^{NHC})Ir(CO)$_2$Cl (13 mg, 70%). Crystals suitable for X-ray diffraction were obtained *via* slow evaporation of a benzene solution. ^{1}H NMR (C_6D_6, 500 MHz): 5.46 [s, 1H of Nitron^{NHC} N−H], 6.84 [t, 1H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz], 6.95−7.25 [m, 12H of Nitron^{NHC}], 8.44 [d, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz]. ^{13}C NMR (C_6D_6): 118.0 [Nitron^{NHC}], 123.5 [Nitron^{NHC}], 125.0 [Nitron^{NHC}], 129.3 [Nitron^{NHC}], 129.4 [Nitron^{NHC}], 130.3 [Nitron^{NHC}], 130.9 [Nitron^{NHC}], 133.4 [Nitron^{NHC}], 137.9 [Nitron^{NHC}], 139.9 [Nitron^{NHC}], 150.4 [Nitron^{NHC}], 168.6 [CO], 174.8 [CO], 180.8 [CN$_2$ of Nitron^{NHC}]. Anal. Calcd for (Nitron^{NHC})Ir(CO)$_2$Cl: C, 44.3; H, 2.7; N, 9.4. Found: C, 45.8; H, 2.8; N, 9.2. IR, solid (cm^{-1}): 3306 (w), 3067 (w), 2066 (vs) [ν(CO)], 1980 (vs) [ν(CO)], 1622 (m), 1602 (m), 1586 (m), 1546 (m), 1494 (m), 1455 (w), 1211 (w), 984 (w), 748 (s), 688 (s), 501 (m). IR, CH_2Cl_2 (cm^{-1}): 2072, 1992.

Synthesis of (Nitron^{NHC})Ir(PPh$_3$)(CO)Cl. A solution of (Nitron^{NHC})Ir(COD)Cl (11 mg, 0.017 mmol) in C_6D_6 (0.7 mL) was treated with PPh$_3$ (5 mg, 0.019 mmol) and transferred to an NMR tube equipped with a J. Young valve, which was degassed *via* a freeze−pump−thaw cycle and then exposed to CO (1 atm). The solution immediately turned a paler yellow color and was shaken for 5 min. After this time, the volatile components were removed *via* lyophilization to afford a pale yellow powder, which was washed with pentane (1 × 2 mL) and dried *in vacuo* to afford (Nitron^{NHC})Ir(PPh$_3$)(CO)Cl (4 mg, 28%). Crystals suitable for X-ray diffraction were obtained *via* slow evaporation of a benzene solution. ^{1}H NMR (C_6D_6): 5.60 [br, 1H of Nitron^{NHC} N−H], 6.83−7.54 [22 H of Nitron^{NHC} and PPh$_3$], 7.78 [m, 6H of PPh$_3$], 8.99 [d, 2H of Nitron^{NHC}, $^3J_{H-H}$ = 8 Hz]. ^{31}P{^{1}H} NMR (CD$_3$CN): 24.1 [s, *P*Ph$_3$]. IR (cm^{-1}): 3053 (w), 1947 (s, [ν(CO)]), 1617 (m), 1601 (m), 1585 (m), 1543 (m), 1495 (m), 1435 (m), 1095 (w), 747 (m), 689 (s), 530 (m), 511 (m). Mass spectrum: m/z 843.0511 (M + 1).

Synthesis of (Nitron^{NHC})$_2$NiBr$_2$. A mixture of NiBr$_2$ (11 mg, 0.050 mmol) and Nitron (34 mg, 0.109 mmol) in acetonitrile (1 mL) was heated at 80 °C for 1 day, thereby resulting in the formation of a pale red-pink precipitate, which was isolated *via* decantation, washed with diethyl ether (1 × 2 mL), and dried *in vacuo* to afford (Nitron^{NHC})$_2$NiBr$_2$ (15 mg, 36%). Red crystals suitable for X-ray diffraction were obtained directly from a less concentrated reaction mixture comprising NiBr$_2$ (2 mg), Nitron (5 mg), and acetonitrile (1 mL). ^{1}H NMR (CD$_3$CN): 6.75 [t, 1H of Nitron, $^3J_{H-H}$ = 7 Hz], 7.19 [t, 2H of Nitron, $^3J_{H-H}$ = 8 Hz], 7.42−7.64 [m, 8H of Nitron], 7.84 [d, 2H of Nitron, $^3J_{H-H}$ = 8 Hz], 7.91 [d, 2H of Nitron, $^3J_{H-H}$ = 8 Hz], 9.36 [broad s, 1H of Nitron N−H] (due to low solubility, the NMR spectrum was obtained by performing the reaction in CD$_3$CN). IR (cm^{-1}): 3331 (m), 3063 (w), 2353 (w), 2320 (w) 1615 (s), 1598 (s), 1584 (s), 1542 (s), 1494 (s), 1452 (m), 1435 (m), 1374 (m), 1318 (m), 1300 (m), 1284 (m), 1257 (m), 1234 (m), 1208 (m), 1028 (m), 976 (m), 893 (m), 747 (s), 686 (s), 457 (m), 427 (m). Mass spectrum: m/z 831.1625 (M + 1).

Synthesis of (Nitron^{NHC})$_2$PdCl$_2$. A mixture of PdCl$_2$ (5 mg, 0.028 mmol) and Nitron (18 mg, 0.058 mmol) was dissolved in CD$_3$CN (1 mL), transferred to an NMR tube equipped with a J. Young valve, and heated at 80 °C for 24 h. After this time, a dark green solution had formed along with the formation of green crystals suitable for X-ray diffraction. The crystals were isolated by decantation, washed with diethyl ether (1 × 2 mL), and dried *in vacuo* to afford (Nitron^{NHC})$_2$PdCl$_2$ (7 mg, 31%). The green crystals obtained from the reaction were suitable for X-ray diffraction. Anal. Calcd for (Nitron^{NHC})$_2$PdCl$_2$: C, 59.9; H, 4.0; N, 14.0. Found: C, 59.4; H, 3.6; N, 14.0. IR (cm^{-1}): 3416 (w), 3288 (m), 3134 (w), 3058 (m), 2064 (w), 1614 (s), 1597 (s), 1583 (s), 1543 (s), 1494 (s), 1468 (s), 1441 (s), 1379 (m), 1322 (m), 1236 (m), 1214 (m), 1072 (m), 1029 (m), 975 (m), 878 (w), 748 (s), 686 (s), 526 (s), 475 (s).

Catalytic Decarboxylation of Formic Acid by (Nitron^{NHC})Ir(CO)$_2$Cl. (a) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (2.1 mg, 0.0035 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with formic acid (19.4 mg, 0.41 mmol) and heated at 80 °C. The reaction was monitored *via* ^{1}H NMR spectroscopy, thereby demonstrating the disappearance of formic acid and the formation of H_2 (TOF = 78 day^{-1}). The vessel can be recharged with formic acid several times and still maintain activity.

(b) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (2.1 mg, 0.0035 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was treated with H^{13}CO$_2$H (6 mg, 0.128 mmol) and heated at 80 °C. The reaction was monitored *via* NMR spectroscopy for 45 h, thereby demonstrating the formation of H_2 and $^{13}CO_2$, as determined by ^{1}H and ^{13}C NMR spectroscopy.

Catalytic Hydrosilylation of Benzaldehyde by PhSiH$_3$ Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (5.6 mg, 0.009 mmol), benzaldehyde (65 mg, 0.612 mmol), and PhSiH$_3$ (17.3 mg, 0.160 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was heated at 60 °C. The reaction was monitored by ^{1}H

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NMR spectroscopy, thereby demonstrating the complete formation of $PhSiH(OCH_2Ph)_2$[168] after 95 min (TOF per Si−H bond = 23 h^{-1}). A separate experiment indicated that $PhSi(OCH_2Ph)_3$ was only formed in significant quantities after many hours at 60 °C.

Catalytic Hydrosilylation of Benzaldehyde by Ph_2SiH_2 Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (5.8 mg, 0.010 mmol), benzaldehyde (20 mg, 0.188 mmol), and Ph_2SiH_2 (28.7 mg, 0.156 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was heated at 60 °C. The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of $Ph_2SiH(OCH_2Ph)$ over a period of 2 h (TOF = 7.8 h^{-1}).

Catalytic Dehydrocoupling between $PhSiH_3$ and $PhCH_2OH$ Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), $PhCH_2OH$ (325 mg, 3.01 mmol), and $PhSiH_3$ (17.3 mg, 0.160 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the rapid consumption of $PhSiH_3$ and the conversion to $PhSiH(OCH_2Ph)_2$, with release of H_2, over a period of 10 min (TOF > 320 h^{-1} per Si−H bond). The reaction was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of $PhSi(OCH_2Ph)_3$ and H_2 over a period of 20 h.

Catalytic Dehydrocoupling between Ph_2SiH_2 and $PhCH_2OH$ Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), $PhCH_2OH$ (100 mg, 0.92 mmol), and Ph_2SiH_2 (22.5 mg, 0.12 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the rapid consumption of Ph_2SiH_2 and the formation of $Ph_2SiH(OCH_2Ph)$, with release of H_2, within 10 min (TOF > 120 h^{-1} per Si−H bond). Monitoring over a period of hours demonstrated the slower subsequent formation of $Ph_2Si(OCH_2Ph)_2$.

Catalytic Dehydrocoupling between $PhSiH_3$ and MeOH Using (Nitron^{NHC})Ir(CO)$_2$Cl. (a) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), MeOH (30 mg, 0.094 mmol), and $PhSiH_3$ (18.2 mg, 0.17 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the complete consumption of $PhSiH_3$ and the conversion to a 12:1 mixture of $PhSiH(OMe)_2$ and $PhSi(OMe)_3$, with release of H_2, within a period of 10 min with subsequent conversion to $PhSi(OMe)_3$ over a period of hours.

(b) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), MeOH (50 mg, 0.094 mmol), and $PhSiH_3$ (18.2 mg, 0.17 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the complete consumption of $PhSiH_3$ and the conversion to a 1:3 mixture of $PhSiH(OMe)_2$ and $PhSi(OMe)_3$, with release of H_2 within a period of 10 min, with subsequent conversion to $PhSi(OMe)_3$ over a period of hours.

(c) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (4 mg, 0.007 mmol) in $PhSiH_3$ (105 mg, 0.97 mmol) was treated with MeOH (127 mg, 3.96 mmol), resulting in the rapid evolution of H_2, which was measured volumetrically (TOF = 195000 h^{-1} for the first 2 equiv).

Catalytic Dehydrocoupling between Ph_2SiH_2 and MeOH Using (Nitron^{NHC})Ir(CO)$_2$Cl. (a) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), MeOH (15 mg, 0.47 mmol), and Ph_2SiH_2 (25 mg, 0.14 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the complete consumption of Ph_2SiH_2 and the conversion to $Ph_2SiH(OMe)$ with release of H_2 within a period of 10 min, with subsequent conversion to $Ph_2Si(OMe)_2$ over a period of 27 h.

(b) A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (4 mg, 0.007 mmol) in Ph_2SiH_2 (110 mg, 0.60 mmol) was treated with MeOH (79.2 mg, 2.47 mmol), resulting in the rapid evolution of H_2, which was measured volumetrically (TOF = 6500 h^{-1} for the first 1 equiv).

Catalytic Transfer Hydrogenation between Pr^{i}OH and PhC(O)Me Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), PhC(O)Me (120 mg, 1.0 mmol), and KOH (1 mg, 0.018 mmol) in Pr^{i}OH (0.7 mL) in an NMR tube equipped with a J. Young valve was heated at 60 °C. The reaction was monitored *via* ^{1}H NMR spectroscopy, thereby demonstrating the formation of PhCH(OH)Me and Me_2CO over a period of 17 h (TOF = 6.5 h^{-1}). After this period, the catalyst was no longer active.

Catalytic Transfer Hydrogenation between MeOH and PhC(O)Me Using (Nitron^{NHC})Ir(CO)$_2$Cl. A solution of (Nitron^{NHC})Ir(CO)$_2$Cl (3 mg, 0.006 mmol), PhC(O)Me (200 mg, 1.66 mmol), and KOH (1 mg, 0.018 mmol) in MeOH (0.7 mL) in an NMR tube equipped with a J. Young valve was heated at 60 °C. The reaction was monitored *via* ^{1}H NMR spectroscopy, thereby demonstrating the formation of PhCH(OH)Me over a period of 18 h (TOF = 2.3 h^{-1}), together with a small quantity of PhC(O)Et (1:8) After this period, the catalyst was no longer active.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00679.

Spectroscopic data (PDF)

Cartesian coordinates for geometry-optimized structures (XYZ)

Accession Codes

CCDC 2038698−2038702 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Malcolm L. H. Green, an amazing chemist and an inspirational mentor.

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