1,2,3-Triazolylidenes as Versatile Abnormal Carbene Ligands for Late Transition Metals

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N-Heterocyclic carbenes (NHCs) have become very popular ligands in transition metal chemistry predominantly due to their efficiency in improving catalyst activities.¹ Their impact, often superior to that of ubiquitous phosphines, has generally been rationalized by the covalent M–C_carbene bond and by the strong donor ability of NHCs.² Arduengo-type imidazolylidenes have been used most widely (A, Chart 1), presumably because the free carbene is extensively stabilized by heteroatoms adjacent to the carbene, which makes them easy to handle.³ Pioneering work by Bertrand and others evidenced that singlet carbenes may be isolated also with less pronounced heteroatom stabilization.⁴a For example, carbenes B–D were analyzed by crystallography.⁴b–d While more reactive E and F have been analyzed in situ.⁴e,f In contrast, abnormal⁵ carbenes such as G have not been characterized in their free form, perhaps due to the small contribution of the carbenic resonance form.⁶ First results indicate that such abnormal carbenes are stronger donors than carbene A–E,⁷ which should provide new opportunities for catalyst design.⁷b,⁸

Here we have applied the [3 + 2] cycloaddition of acetylenes with azides ("click" chemistry) as a versatile and flexible method⁹ for synthesizing heterocycles that are effective precursors for a new class of abnormal carbenes, thus greatly expanding the family of carbene ligands. Substitution of 1,2,3-triazoles at the 1- and 4-position is virtually unlimited due to the accessibility of a large variety of acetylenes and azides.¹⁰ Copper-mediated cyclization allows for introducing functional groups into the triazole framework for diverse purposes, e.g., for surface functionalization, bioconjugate immobilization, or supramolecular applications.¹¹ We have used the simple triazoles 1a and 1b for further ligand synthesis (Scheme 1). Alkylation of the 3-position using MeI was regioselective for the simple triazoles 1a. Alkylation of the 3-position using MeI was regioselective for the simple triazoles 1a and 1b, respectively. A cis arrangement of the CO ligands was evidenced from a crystal structure determination of 7b (Figure 2b). Retention of this conformation in solution is supported by the presence of two inequivalent signals in the ¹³C NMR spectrum. Assignment of the carbonyl resonances was facilitated by ligand exchange reactions using isotopically labeled ¹³CO. This allowed the metal-bound triazolylidene carbon to be unambiguously identified, δC 161.2 in 6b and 162.0 in 7b. The small ¹⁰³Rh–¹³C coupling constant in 6b (JRhC = 39.4 Hz) suggests a relatively weak Rh–Cwz bond.¹⁵

The CO stretch vibrations of the iridium complex 7b (νw = 2062 cm⁻¹, νs = 1979 cm⁻¹) provide a direct probe for the donor

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properties of the triazolylidene ligand. For complexes of the type
IrCl(CO)L, a linear correlation between ν\text{average}(CO) and the Tolman
electronic parameter (TEP) of L has been established.16 Using linear
regression methods, a TEP(trz) = 2047.4 cm\(^{-1}\) has been calculated
for 7b. This value compares well with the most basic 2-imida-
zoxylidenes A (e.g., TEP(ICy) = 2049.6; ICy = N,N\text{′}-dicyclohexy-
limidazol-2-ylidene), though it is higher than the TEP of other
abnormal carbenes.16a The donor properties of the trz ligand may
be further modified by adjusting the substitution pattern of the
heterocycle, thus filling the gap between the most basic normal
and abnormal carbenes.

In summary, 1,3,4-substituted 1,2,3-triazolium salts are readily
accessible and highly modular precursors for the synthesis of new
abnormal NHC complexes with a variety of transition metals. The
triazole framework is particularly versatile for introducing substit-
uents (e.g., chelating groups) and functionalities such as dendritic
supports or molecular recognition sites. Considering this flexibility
in ligand synthesis, the versatility of metal insertion, and the high
impact of abnormal carbenes in catalysis, abnormal triazolylidene
complexes are expected to have great potential for the development
of new catalysts with unprecedented ligand-induced reactivity
patterns.

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**Note Added after ASAP Publication.** IR data for 7b were corrected
in the version published October 8, 2008.

**Supporting Information Available:** Experimental procedures and
spectroscopic data for all reported complexes, and CIF files for
structures 3b, 6a, and 7b. This material is available free of charge via
the Internet at http://pubs.acs.org.

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