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Transition Metal Migration upon Attempting the Wolff Rearrangement of an Ir(III) Five-Membered Metallacycle

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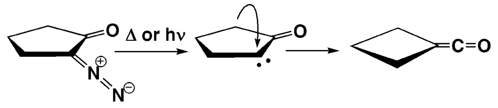
One of the most important applications of the Wolff rearrangement is the synthesis of cyclobutanes from α,β-diazocyclopentanones.[1,2] This ring contraction is triggered by the thermal or photochemical extrusion of N_2, then followed by migration of the C atom directly bonded to the keto group to the resulting carbene (Scheme 1). The starting diazo compounds can be prepared from the corresponding α-formyl ketones and tosyl azide in basic media and are generally stable molecules that often require transition metal additives for their smooth thermal decomposition.[3] Transition metal organometallic versions of the Wolff contraction are unknown, to the best of our knowledge, but we now report that the α-formyl-3-iridacyclopentanone **1** (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) of Scheme 2 undergoes an unusual rearrangement to yield the contracted four-membered iridacycle **5** when treated with TsN_3.[4]

Compound **1** is obtained from the known 3-iridacyclopentene **2**,[5] by the series of sequential steps represented in Scheme 2, and appears to exist in $CDCl_3$ solutions as the hydroxymethylene tautomer exclusively.[6] Doubtless, the inert character of the iridium ligand bonds of **2** plays a decisive role in the success of this synthetic methodology. Stereo- and regioselectivity are also important issues. This is shown by the syn position of the hydroxyl group of **3** with respect to the Ir−CO linkage that reveals that the hydroboration of the C═C bond of the metallacycle occurs on the less congested face, namely, that opposite to the IrN_3 face of **2**, and by the generation of only one formyl product **1**, namely, that in β with respect to the metal. All of the complexes herein described have been characterized by microanalysis and spectroscopy (see Supporting Information).

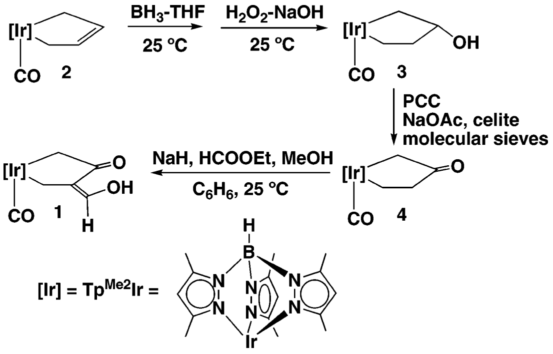
Treatment of compound **1** with TsN_3 (CH_2Cl_2, NEt_3, 25 °C) gives the four-membered iridacycle **5** (Scheme 3) instead of the diazoalkane **A**, where the latter appears to be only a reactive intermediate in the path leading to **5**.[7] Most notably, from the structure of **5** (isolated in 60% yield), it is evident that attack of the iridium center to the carbene carbon of **B** is preferred over the alternative attack of the carbon atom. This is an important finding because heteroatom migration that is preferential over carbon migration under Wolff reaction conditions is very uncommon,[1,8] to the point that transition metal migration is in fact unprecedented.

Figure 1 shows the X-ray structure of **5**, which reveals the planarity of the iridacyclobutanone ring and the conjugation of the C═C and C═O bonds (dihedral angle 21(5)°). Interestingly, the simplest organic analogue of **5** (CH_2 instead of the isolobal $Tp^{Me2}Ir(CO)$ fragment) is a liquid very prone to polymerization.[9]

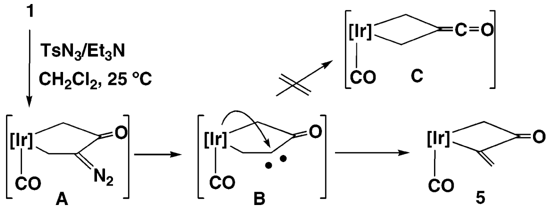
Scheme 1. Wolff Rearrangement of α,β-Diazocyclopentanone



Scheme 2. Synthesis of Compound **1**



Scheme 3. Formation of Compound **5**



Scheme 4. Some Reactions of Complex **5**

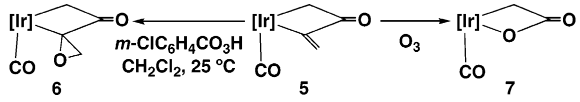
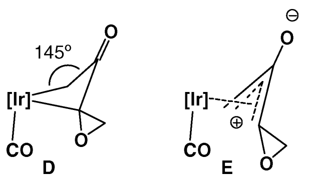


Chart 1



Complex **5** exhibits striking reactivity (Scheme 4). Despite its α-keto olefinic constitution, it readily undergoes epoxidation[10] by the electrophilic reagent, *m*-chloroperbenzoic acid, to yield compound **6**. It appears that the metal center bound to the cyclic olefin carbon atom overcompensates the electron-withdrawing effect of the C═O unit. The stereochemistry of **6**, deduced from NOESY experiments and confirmed by X-ray studies (Figure 2), demonstrates that the peracid attacks the less congested face of the olefin

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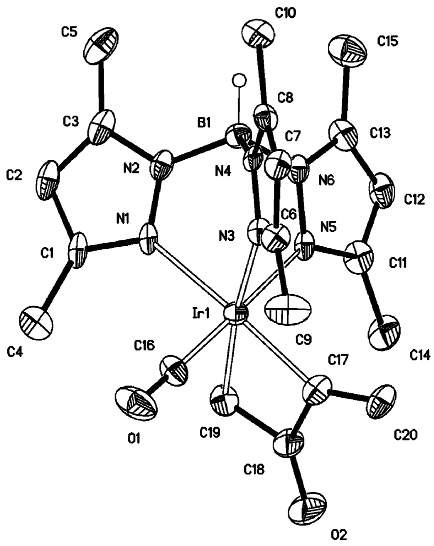

Figure 1. ORTEP representation for the molecular structure of compound **5** (30% ellipsoids). Selected bond lengths (Å) and angles (deg): Ir−C(17) 2.02(2), C(17)−C(20) 1.25(3), C(18)−O(2) 1.29(3); C(17)−Ir−C(19) 72.2(5), Ir−C(17)−C(20) 145(2).

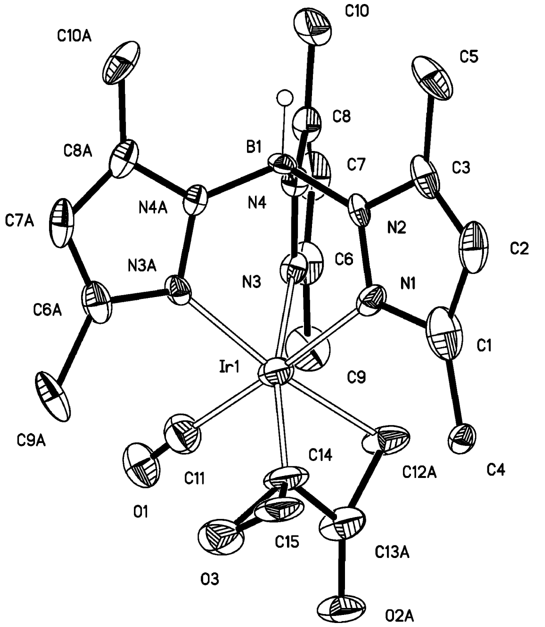

Figure 2. ORTEP representation for the molecular structure of compound **6** (30% ellipsoids). Selected bond lengths (Å) and angles (deg): Ir(1)−C(14) 1.910(16), Ir(1)−C(12) 2.146(16), C(13)−O(2) 1.264(15); C(14)−Ir(1)−C(12)A 75.4(9), O(2)A−C(13)A−C(12)A 135.0(13).

(i.e., that syn to the Ir−CO unit). The four-membered ring of **6** is no longer planar (**D**, Chart 1), probably as a reflection of the contribution from canonic form **E**.[11] Finally, upon ozonolysis, the iridalactone[12] **7** (Figure 3) is obtained, following a process that finds precedent in the ozonolysis of conjugated keto olefins.[13]

In conclusion, well-known organic transformations of cyclic molecules become markedly different for metallacycles, that is, the presence of a transition metal within the ring has a dramatic effect on its reactivity. Further studies along this line are in progress and will be reported in due course.

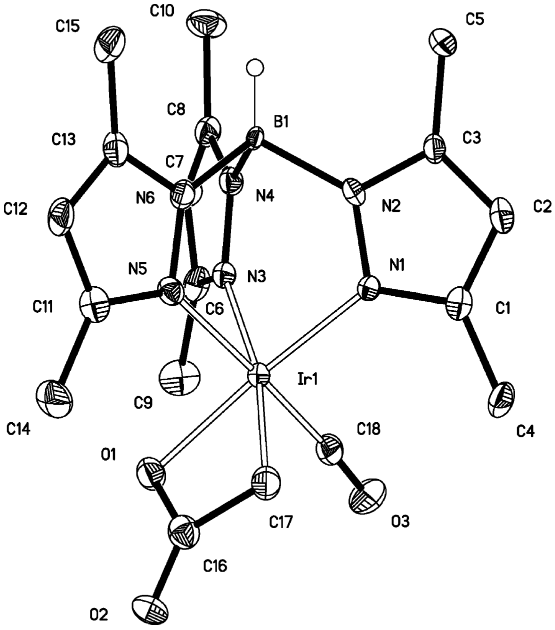

Figure 3. ORTEP representation for the molecular structure of compound **7** (30% ellipsoids). Selected bond lengths (Å) and angles (deg): Ir(1)−C(17) 2.073(8), C(16)−C(17) 1.531(12), O(2)−C(16) 1.198(10); C(18)−Ir(1)−C(17) 89.1(4), O(1)−Ir(1)−C(17) 67.2(3).

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Supporting Information Available: PDF file with synthetic procedures and spectroscopic and analytical data for all new complexes, structure and refinement data, and X-ray crystallographic file in CIF format (compounds **5**−**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Although **A** has not been detected, it seems to us that its formation and fast rearrangement to carbene **B** is a simple, reasonable explanation for the generation of **5**.
(8) As stated in ref 1, in the *photochemical* version of the Wolff rearrangement, carbon migration is preferred over heteroatom migration, with the following order of reactivity: $H > alkyl \geq aryl > SR > OR \geq NR_2$. Naturally, when there is no alternative, heteroatom migration gives the expected ketene or derivatives therefrom. For the *thermal* process, heteroatom migration is seldom observed, although we have found a case of preferential S migration over a CMe_2 group in a five-membered thiocycle to give a α-keto olefin related to **5**. See: Bolster, J.; Kellogg, R. M. *J. Org. Chem.* **1980**, *45*, 4804.
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