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New Pd-catalyzed tandem cyclization processes on group 6 bis-carbene complexes

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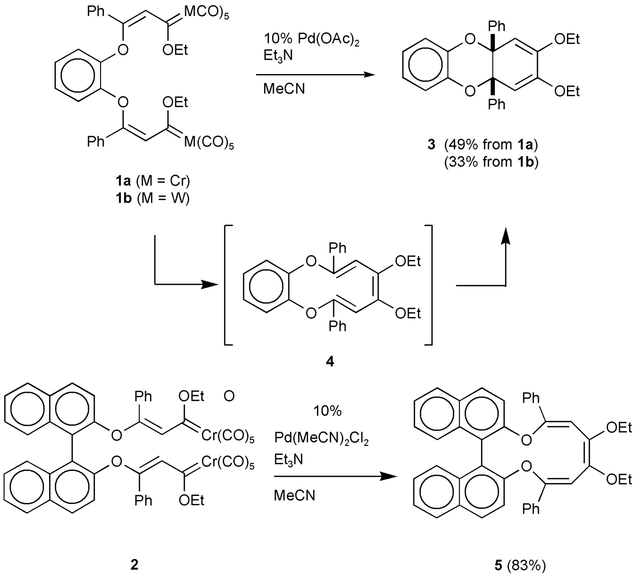
The reaction of bis-carbene complexes 1a,b derived from catechol and Pd-catalysts gave product 3 derived from an intramolecular coupling–electrocyclization process, while nucleophilic attack–*NH*-carbene insertion product 6 was obtained from complexes 1c,d derived from 1,2-diaminobenzene.

Tandem reactions on chromium(0) carbene complexes are well known processes.[1] In fact, one of the most appealing features of these compounds is their ability to effect complex transformations in a single step. The most representative of such cascade reactions is Dötz's benzannulation.[1e,2] This, and other related processes rest in the ability of chromium to generate reactive intermediates which are thereafter trapped by the reagents in the reaction medium to produce the reaction products.

Recently, we have demonstrated that the reactivity of group 6 alkoxy- and aminocarbene complexes can be increased by using Pd-catalysts.[3] Other reactions of group 6 carbene complexes induced by their catalytic transmetallation to Pd[4] and Rh-complexes[5] were described after our original report.[3a] Recently, a Cu–carbene complex has been characterized in the transmetallation reaction from a chromium(0) carbene complex to a Cu-complex.[6] Reported herein are the preliminary results obtained in the catalytic reactions of group 6 homobimetallic-bis-carbene complexes.[7]

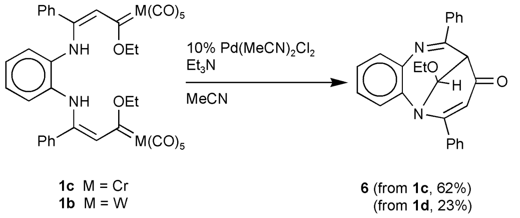
The complexes **1** and **2** used in this study were prepared by double Michael addition of aromatic dinucleophiles to pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium(0) or tungsten(0).[8] Complex **1a** was reacted with Pd(OAc)$_2$ at RT to form compound **3** as a single isomer. Pure compound **3** was obtained after column chromatography.[9] Compound **3** should arise from the initial dimerization product, namely cyclohexatriene **4**, that spontaneously cyclized to diene **3**. This was demonstrated by reacting bis-carbene complex **2** and Pd(MeCN)$_2$Cl$_2$. In this case hexatriene **5** was obtained. This compound was stable even under heating. Clearly, the cyclization of compound **5** would form a highly strained diene and thence the cyclization stops at the triene stage (Scheme 1). The reaction of tungsten bis-carbene derivative **1b** and Pd(OAc)$_2$ also produced tricycle **3** in an analogous process (Scheme 1).

Treatment of complex **1c** derived from *o*-diaminobenzene with Pd(MeCN)$_2$Cl$_2$ gave a new compound whose structure is not the nitrogen analogous to the tricycle **3**. Thus, instead of the single resonance attributable to the vinyl ether moiety of **3** (δ = 4.79 ppm) or **5** (δ = 4.59 ppm), three new resonances (δ = 5.49 (s); 5.29 (d, J = 2.5 Hz); 4.62 (d, J = 2.5 Hz) ppm), appear in the ^{1}H NMR spectrum of this compound. Thus, a different process has occurred with complex **1c**. A single monocrystal was submitted to X-ray diffraction analysis unambiguously establishing the structure of this new compound as the tricycle **6** (Scheme 2, Fig. 1).[10] Tungsten bis-carbene complex gave also tricycle **6** under analogous conditions.



Scheme 1

The results depicted in Scheme 2 show that the reaction of bis-carbene complexes **1** yields very different products, depending on the heteroatom attached to the metallatetraene moiety, and on the size of the ring formed after the initial cyclization. In



Scheme 2

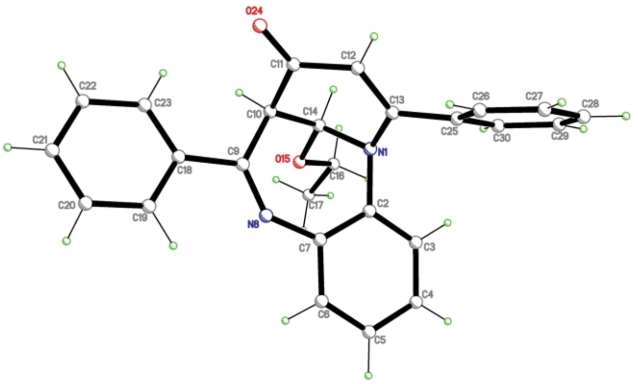


Fig. 1 Crystal structure for compound **6** obtained from **1c**.

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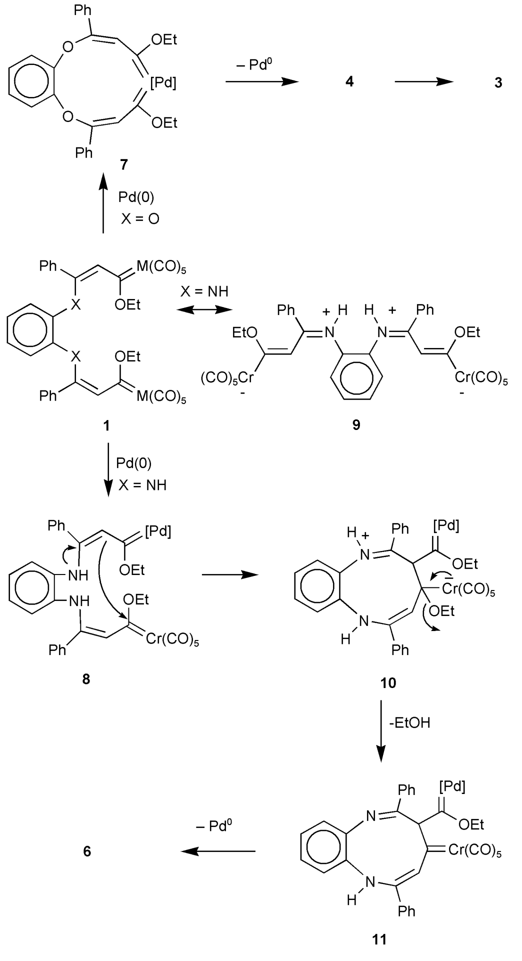
this way, for oxygenated substituents, the reaction follows, as previously proposed by us,[3b] an intramolecular cyclization pathway through a mononuclear Pd–bis-carbene complex **7** (Scheme 3). The differences between the reaction products would depend exclusively on the ability of the initially formed cyclohexatriene to experiment the subsequent electrocyclization. The situation is different for complexes **1c**,**d**. In these cases the first transmetallation would form intermediate **8**. The nine membered ring present in the final product **6** would be closed on this heterobimetallic bis-carbene. In fact, while the β-carbon of the enamine moiety of the starting material is not nucleophilic enough to attack the second carbene carbon, (probably due to the strong participation of forms like **9**), the Pd–carbene **8** may have its electron acceptor capacity strongly reduced. This would be expected for a late transition metal without electron-withdrawing ligands.[11] Hence, the enamine carbon of this moiety becomes nucleophilic enough to attack the remaining chromium–carbene carbon and form intermediate **10**. Intermediate **10** would lose EtOH to yield the new heterobimetallic bis-carbene **11**. Intermediate **11** yields the final product **6** by NH-insertion followed by elimination of Pd(0) and final oxidation of the metal-moiety (Scheme 3).

From these results it is clear that the transmetallation from Cr- or W- to Pd not only enhances the reactivity of chromium(0) or tungsten(0) (Fischer) carbene complexes in reactions such as dimerization and CH insertion,[3] but it is also able to promote previously unknown processes by decreasing the ability of the metal center to accept electrons. In addition, it has to be noted that in all the processes discussed, final products **3** and **6** were obtained as a single isomer.

In conclusion, the reaction of bis-carbene complexes (represented by **1** and **2**) and Pd-catalysts produces different polycyclic products, through cascade processes, depending on the nature of the tether joining both metallic centers. In this way intramolecular coupling–electrocyclization (for oxygen tethers) sequences, or nucleophilic attack–*NH*-carbene insertion (for nitrogen tethers), can be observed. Thus, the coupling Cr– or W–carbene–Pd catalyst leads to new, potentially useful cascade processes. Further work on these and other related cascade cyclization reactions are being pursued in our laboratories.



Scheme 3

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9 The experimental procedure for the reaction of complex **1a** to form tricycle **3** is representative of the methodology followed through this work: 300 mg (0.37 mmol) of bis-carbene complex **1a** was dissolved in MeCN (2 mL). To this solution was added $Pd(OAc)_2$ (8.3 mg, 0.037 mmol) and Et_3N (41 mg, 0.41 mmol). The reaction mixture was stirred for 2 h at RT until the disappearance of the starting material (checked by TLC). The solvent was distilled under reduced pressure and the residue was dissolved in EtOAc and filtered through Celite. The solvent was removed *in vacuo* and 230 mg of a brown crude reaction mixture were obtained. Flash column chromatography (SiO_2, 20 : 1 Hexane : EtOAc) yielded 77 mg (49%) of **6a** as a white solid. ^1H NMR (200 MHz): δ 7.11–6.73 (m, 14H, ArH), 4.79 (s, 2H, CH), 3.75 (m, 4H, OCH_2), 1.29 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (75 MHz) δ 152.0 (Cq), 145.5 (Cq), 138.9 (C*ipso*), 127.8, 127.5, 127.1, 120.9, 116.3 (aromatic CH), 102.4 (CH), 83.4 (Cq), 63.7 (OCH_2), 14.0 (CH_3). IR (CCl_4): ν 1616, 1603, 1493, 1273 cm^{-1}. $C_{28}H_{26}O_4$: Calcd C 78.85, H 6.14. Found: C 79.06, H 6.32%.

10 *Crystal data*: $C_{26}H_{22}N_2O_2$, M = 394.46, monoclinic, $C2/c$, a = 27.815(3) Å, b = 10.620(1) Å, c = 18.243(2) Å, β = 129.124°, V = 4180.6(9) Å^3, T = 296 K, Z = 8, ρ = 1.243 mg m^{-3}, μ = 0.08 mm^{-1}, $F(000)$ = 1664. 10720 measured reflections were collected on a SMART CCD-BRUKER diffractometer, 3682 independent reflections (Rint = 0.0637), 290 refined parameters, final R indices [$I > 3\sigma(I)$], $R1$ = 0.0468, $wR2$ = 0.0945. CCDC 167018. See http://www.rsc.org/suppdata/cc/b2/b204907d/ for crystallographic files in CIF or other electronic format.

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