



## C–C Activation Hot Paper

## Oxidative Addition of a Mechanically Entrapped C(sp)–C(sp) Bond to a Rhodium(I) Pincer Complex

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**Abstract:** By use of a macrocyclic phosphinite pincer ligand and bulky substrate substituents, we demonstrate how the mechanical bond can be leveraged to promote the oxidative addition of an interlocked 1,3-diyne to a rhodium(I) center. The resulting rhodium(III) bis(alkynyl) product can be trapped out by reaction with carbon monoxide or intercepted through irreversible reaction with dihydrogen, resulting in selective hydrogenolysis of the C–C  $\sigma$ -bond.

With many prospective applications in organic chemistry, the selective cleavage of carbon-carbon single bonds is a highly coveted disconnection. Insertion of a transition metal into these linkages is a conceptually simple and attractive method but typically associated with unfavorable thermodynamics and orbital directionality, with the latter conferring high activation barriers that allow alternative metal-based reactivity.<sup>[1]</sup> Whilst considerable progress has been made exploiting chelation to a metal and the relief of ring strain as a driving force, the organometallic chemistry of other C–C  $\sigma$ -bond activation reactions is considerably underdeveloped.<sup>[1,2]</sup>

The strongest C–C  $\sigma$ -bonds are found in 1,3-diyne, with buta-1,3-diyne characterized by a single bond dissociation energy of  $670 \pm 8 \text{ kJ mol}^{-1}$ : nearly twice that of ethane.<sup>[3]</sup> Reactions involving scission of C(sp)–C(sp) bonds have been reported in the literature, although they are almost exclusively associated with binuclear metallocene and metal cluster systems, where  $\mu_2$ -coordination of the diyne is implicit in the outcome.<sup>[4]</sup> Mononuclear examples are limited to work by Hill et al. who reported the oxidative addition of tungsten alkylidyne terminated 1,3-diyne to a reactive ruthenium(0) fragment derived from Roper's complex,  $[\text{Ru}(\text{PPh}_3)_3(\text{CO})_2]$ .<sup>[5]</sup> In these isolated examples the substrate substituents play a decisive role and attempts to replicate this reactivity using diphenylbutadiyne proved unsuccessful.<sup>[6]</sup>

Inspired by reports of unique metal-based reactivity using interlocked ligands<sup>[7,8]</sup> and as part of our research exploring

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the organometallic chemistry of macrocyclic pincer complexes,<sup>[9,10]</sup> we speculated that mechanical entrapment could be exploited to overcome the unfavorable kinetics associated with C(sp)–C(sp) bond oxidative addition relative to substitution of the diyne, and enable onward reactivity of the resulting bis(alkynyl) products to be explored. We herein describe work evaluating this hypothesis using rhodium complex **1**, which features a macrocyclic phosphinite pincer ligand (POCOP-14)<sup>[9]</sup> and bulky aryl terminated 1,3-diyne ( $\text{Ar}'\text{C}_4\text{Ar}'$ ,  $\text{Ar}' = 3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3$ ; Scheme 1).

The synthesis of **1** was achieved by reaction of *trans*- $[\text{Rh}(\text{POCOP-14})\text{Cl}_2(\text{CO})]$ <sup>[9]</sup> with  $\text{Ar}'\text{C}_2\text{MgCl-LiCl}$  and  $\text{Me}_3\text{NO}$  promoted decarbonylation of the resulting bis(alkynyl)carbonyl complex **3** (Scheme 2, insert).<sup>[11]</sup> The five coordinate intermediate **2** invoked in the latter step was not observed when the reaction was monitored in situ by NMR spectroscopy and in the absence of a decarbonylation agent **3** is thermally stable under an Ar atmosphere (363 K, 16 h,  $[\text{D}_8]$ toluene).<sup>[12]</sup> The formation of **1** in this manner parallels active metal template methods pioneered by Leigh for the capture of interlocked molecules and demonstrates the endergonic nature of the proposed C(sp)–C(sp) bond oxidative addition.<sup>[13,14]</sup>

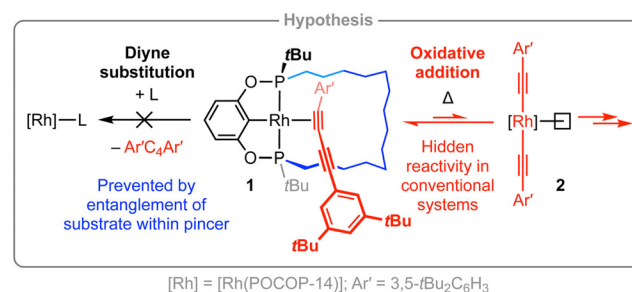
Complex **3** was characterized in  $[\text{D}_8]$ toluene solution by NMR spectroscopy and is notable for the adoption of  $C_2$  symmetry, a  $^{31}\text{P}$  resonance at  $\delta$  188.1 ( $^1J_{\text{RhP}} = 92 \text{ Hz}$ ), and alkynyl carbon signals at  $\delta$  95.4 ( $\text{Rh-C}\equiv\text{C}$ ;  $^1J_{\text{RhC}} = 35 \text{ Hz}$ ,  $^2J_{\text{PC}} = 15 \text{ Hz}$ ) and 111.6 ( $\text{Rh-C}\equiv\text{C}$ ;  $^2J_{\text{RhC}} = 7 \text{ Hz}$ ). Installation of the alkynyl ligands and retention of the carbonyl was further substantiated by analysis in the solid state by single-crystal X-ray diffraction (Scheme 2) and IR spectroscopy ( $\nu(\text{C}\equiv\text{C})_{\text{ATR}} = 2105 \text{ cm}^{-1}$  (asymmetric);  $\nu(\text{C}\equiv\text{O})_{\text{ATR}} = 2066 \text{ cm}^{-1}$ ).

The transformation of **3** into **1** was corroborated in a similar manner, although the product is fluxional in solution on the NMR timescale (600 MHz). Time averaged  $C_2$

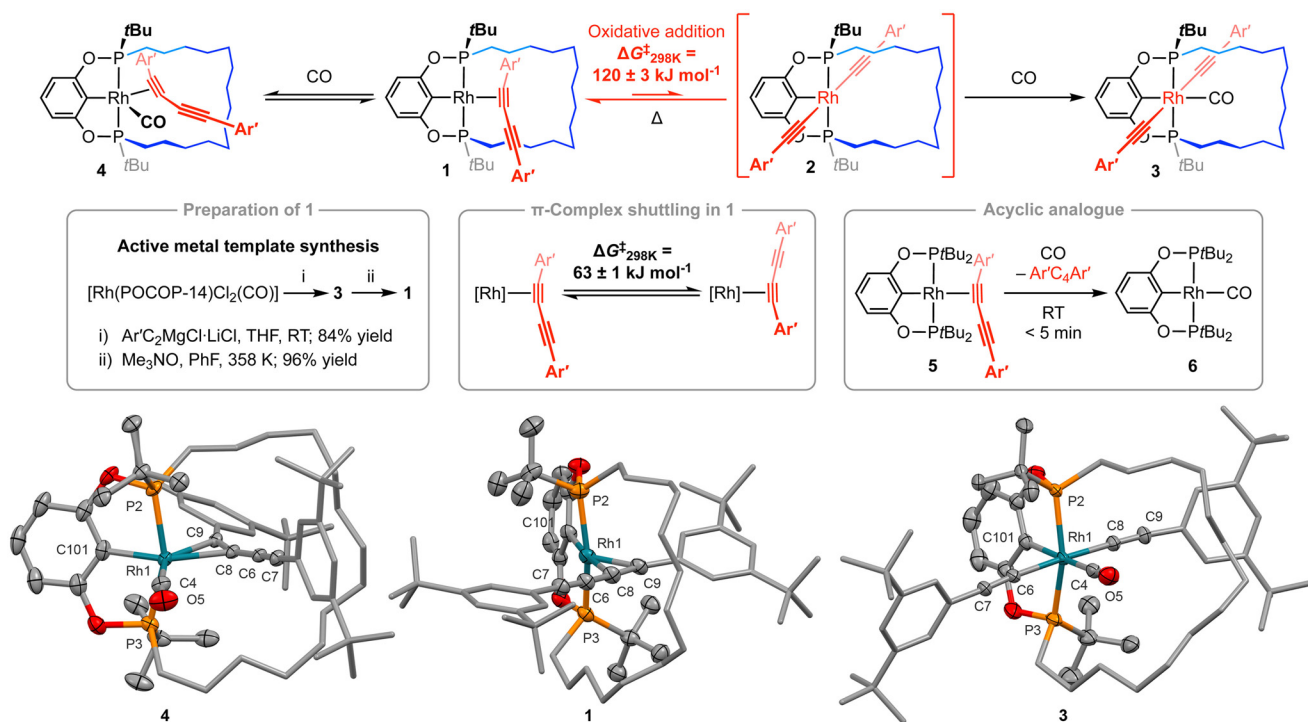
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**Scheme 1.** Structure and hypothesized reactivity of **1**, involving C(sp)–C(sp) bond oxidative addition of a mechanically entrapped diyne and formation of **2**.



**Scheme 2.** Reaction of **1** with carbon monoxide and related chemistry. Unless otherwise stated, reactions were performed in toluene/ $[\text{D}_8]$ toluene under argon or carbon monoxide (1 atm). Solid-state structures of **1** (not unique,  $Z' = 2$ ), **3** and **4** depicted with selected thermal ellipsoids at 50% probability; minor disordered components, hydrogen atoms, and solvent molecules omitted. Animated structures are also provided in the Supporting Information. Selected bond lengths [Å] and angles [°]: **1** as shown, Rh1–P2 2.2579(11), Rh1–P3 2.3041(11), P2–Rh1–P3 158.55(4), Rh1–C101 2.006(4), Rh1–Cnt(C8,C9) 2.072(4), C6–C7 1.202(6), C6–C8, 1.379(6), C8–C9, 1.243(6); C101–Rh1–Cnt(C8,C9) 160.12(13), C6–C8–C9 169.3(4); other unique cation, Rh11–P12 2.2522(11), Rh11–P13 2.3082(11); P12–Rh11–P13 157.94(4); Rh11–C201 2.005(4), Rh11–Cnt(C48,C49) 2.071(3); C201–Rh1–Cnt(C48,C49) 161.7(2), C46–C47 1.203(6), C46–C48 1.384(6); C48–C49 1.244(6), C46–C48–C49 168.3(4); **3**: Rh1–P2 2.3133(4), Rh1–P3 2.3539(5), P2–Rh1–P3 156.50(2), Rh1–C101 2.037(2), Rh1–C4 1.955(2), C101–Rh1–C4 172.71(8), Rh1–C6 2.037(2), Rh1–C8 2.045(2), C6–Rh1–C8 177.33(7), C6–C7 1.204(3), C8–C9 1.204(3); **4**: Rh1–P2 2.2935(5), Rh1–P3 2.3273(5), P2–Rh1–P3 155.32(2), Rh1–C101 2.066(2), Rh1–C4 1.942(2), C101–Rh1–C4 106.01(8), Rh1–Cnt(C8,C9) 2.0482(12), C101–Rh1–Cnt(C8,C9) 135.41(7), C6–C7 1.205(3), C6–C8 1.384(2), C8–C9 1.270(3), C6–C8–C9 163.3(2); Cnt = bond centroid.<sup>[22]</sup>

symmetry at 298 K is implied by a single sharp  $^{31}\text{P}$  resonance at  $\delta$  184.8, which displays enhanced coupling to  $^{103}\text{Rh}$  ( $J_{\text{RhP}} = 162 \text{ Hz}$ ) compared to **3**, consistent with the reduced coordination number.<sup>[15]</sup> This signal broadened on cooling, but decoalescence was not achieved at 183 K. The structural dynamics are more readily interrogated using variable temperature  $^1\text{H}$  NMR spectroscopy (183–363 K), with the  $C_1$  symmetry expected for binding of  $\text{Ar}'\text{C}_4\text{Ar}'$  through one of the alkynes observed at 298 K. Subsequent line shape analysis enabled deconvolution of the dynamics into restricted rotation of the bound alkyne  $\text{Ar}'$  substituent ( $\Delta H^\ddagger = 50.1 \pm 0.5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -39 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger_{298\text{K}} = 62 \pm 1 \text{ kJ mol}^{-1}$ ) and  $\pi$ -complex shuttling ( $\Delta H^\ddagger = 75.2 \pm 0.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +40 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger_{298\text{K}} = 63 \pm 1 \text{ kJ mol}^{-1}$ ; Scheme 2, insert).<sup>[16]</sup> The characteristics of the latter are consistent with a dissociative mechanism. Use of the isotopologue  $[\text{Rh}(\text{POCOP-14})(\eta^2\text{-Ar}'\text{C}^{13}\text{C}_2\text{CAr}')] \text{ (}^{13}\text{C-1)}$  enabled location of the  $^{13}\text{C}$  resonances associated with the C(sp)–C(sp) bond at  $\delta$  83.0 (free) and 70.9 (bound). The corresponding  $^1J_{\text{CC}}$  coupling constant of 156 Hz is large, but in-line with expectation for bonds of this nature.<sup>[17]</sup> Analysis of **1** in the solid state by single-crystal X-ray diffraction confirmed  $\eta^2$ -coordination of the diyne, although it is

appreciably skewed to one side of the coordination plane as a consequence of steric buttressing of the substituents with the tetradecamethylene strap (C–Rh–alkyne = 160.12(13)/161.7(2)°, Scheme 2). Two alkyne stretching bands of substantially different frequency were also determined in the solid state by IR spectroscopy, *viz.*  $\nu(\text{C}\equiv\text{C})_{\text{ATR}} = 1938$  (bound), 2154 (free)  $\text{cm}^{-1}$ .

To probe the effect of diyne entanglement within the macrocyclic pincer ligand, a solution of **1** in  $[\text{D}_8]$ toluene was placed under an atmosphere of CO at RT. Five coordinate carbonyl complex **4** ( $\delta_{31\text{P}} = 195.2, 182.5$ ;  $^2J_{\text{PP}} = 420 \text{ Hz}$ ;  $\nu(\text{C}\equiv\text{C})_{\text{ATR}} = 1863$  (bound), 2159 (free)  $\text{cm}^{-1}$ ;  $\nu(\text{C}\equiv\text{O})_{\text{ATR}} = 1975 \text{ cm}^{-1}$ ) was formed in quantitative spectroscopic yield and subsequently isolated from solution (Scheme 2). This complex can be viewed as an intermediate in the associative substitution of  $\text{Ar}'\text{C}_4\text{Ar}'$  by CO, but dissociation of the diyne in this case appears to be arrested by the steric constraints imposed by tight confinement within the ring. For comparison, the acyclic congener of **1**,  $[\text{Rh}(\text{PONOP-}t\text{Bu})(\eta^2\text{-Ar}'\text{C}_4\text{Ar}')\text{CO}]$  **5** (see Supporting Information for full details),<sup>[18]</sup> was prepared and found to give Rh<sup>I</sup> carbonyl derivative **6** by rapid displacement of the diyne upon placing under CO (1 atm) at RT.<sup>[19,20]</sup> Coordination of CO to **1** is reversible and

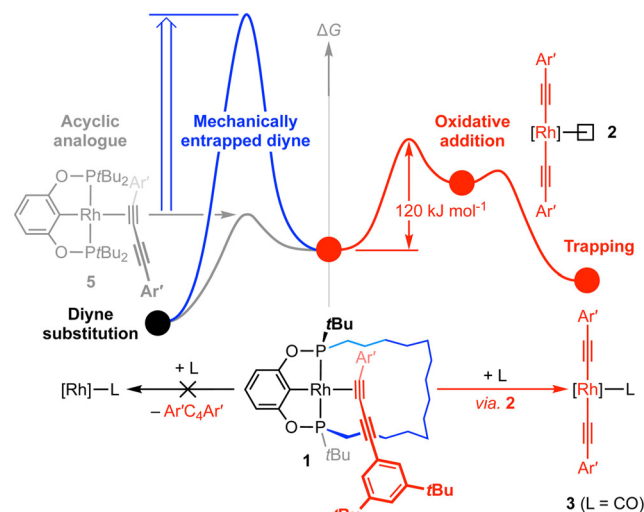
analysis of the dynamic equilibrium between **1** and **4** by variable temperature UV-vis spectroscopy (1 atm CO) enabled the associated thermodynamic parameters to be established ( $\Delta H = -71 \pm 1 \text{ kJ mol}^{-1}$ ,  $\Delta S = -223 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1}$ ).<sup>[21]</sup> These values notably indicate that the reaction of **1** with CO becomes endergonic above  $T = 318 \text{ K}$ .

Pertinent to the overarching hypothesis, prolonged thermolysis of equilibrium mixtures of **1/4** in toluene under CO resulted in quantitative formation of **3** (Scheme 2). The kinetics of this remarkable transformation were studied using UV-vis spectroscopy between 353–373 K ( $[\text{Rh}] = 0.2 \text{ mM}$ ; 1 atm CO,  $\approx 9 \text{ mM}$ ). Under these conditions equilibration between **1** and **4** is fast and the former is the major Rh<sup>I</sup> component ( $> 60\%$ ). The formation of **3** follows first order kinetics and is independent of CO pressure (1.0–1.3 atm;  $t_{1/2} = 4.5 \text{ h}$  at 358 K). Taken together these data are consistent with a two-step mechanism from **1** involving reversible and rate-determining C–C  $\sigma$ -bond oxidative addition to afford **2**, followed by fast and irreversible CO coordination to yield **3**. Supporting this conclusion, a primary kinetic isotope effect of  $1.08 \pm 0.02$  was measured for **1**/<sup>13</sup>C-**1** at 373 K. The associated activation parameters ( $\Delta H^\ddagger = 123 \pm 2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +9 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger_{298\text{K}} = 120 \pm 3 \text{ kJ mol}^{-1}$ ) are congruent with the mechanism and, by reference to those established for  $\pi$ -complex shuttling in **1**, enable a barrier of  $\Delta G^\ddagger_{298\text{K}} \approx 57 \text{ kJ mol}^{-1}$  to be attributed to the oxidative addition.

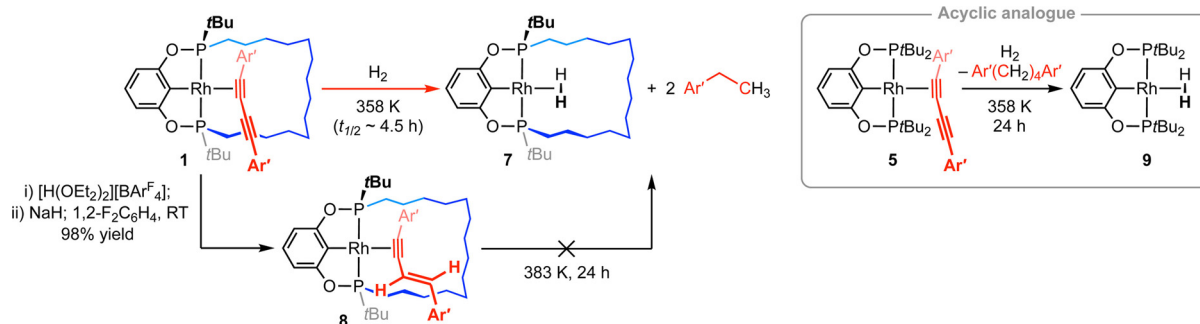
Further supporting the equilibrium formation of **2**, heating a solution of **1** in [D<sub>8</sub>]toluene under H<sub>2</sub> (1 atm) at 358 K resulted in formation of dihydrogen complex **7** ( $\delta_{31\text{P}} 198.3$ ,  $^1J_{\text{RhC}} = 165 \text{ Hz}$ ),<sup>[9]</sup> with concomitant generation of two equivalents of Ar'<sup>2</sup>CH<sub>2</sub>CH<sub>3</sub> (24 h, Scheme 3). This outcome is fully consistent with a reaction sequence involving rate-determining insertion of the metal into the C(sp)–C(sp) bond followed by hydrogenolysis, and notably occurs with a similar rate to the formation of **3** from **1** in the presence of excess CO at 358 K ( $t_{1/2} \approx 4.5 \text{ h}$ ). To exclude alternative reaction pathways commencing with hydrogenation of the diyne, the *E*-enyne derivative **8** ( $\delta_{31\text{P}} 185.1, 182.5$ ;  $^2J_{\text{PP}} = 401 \text{ Hz}$ ) was prepared by stepwise proton and hydride transfer and shown to be thermally stable under H<sub>2</sub> (1 atm). The decisive role of macrocyclic ligand in **1** was also confirmed by comparison to the acyclic congener **5**, with Ar'(CH<sub>2</sub>)<sub>4</sub>Ar' the only organic product observed alongside Rh<sup>I</sup> dihydrogen complex **9** on

reaction with H<sub>2</sub> under equivalent conditions (Scheme 3, insert).<sup>[20]</sup>

The remarkable reactivity of **1** presented herein can be reconciled by a pronounced “catenand effect”, the name given by Sauvage for the augmentation of a metal ion’s reactivity due to confinement within a threaded structure,<sup>[7]</sup> and this conclusion is substantiated by comparison to the electronically similar acyclic congener **5** (Scheme 4).<sup>[9,18]</sup> Insertion of rhodium into the C(sp)–C(sp) bond of Ar'<sup>2</sup>C<sub>4</sub>Ar' in **1** is a reversible but thermodynamically uphill reaction that is associated with a formidable activation barrier of  $\Delta G^\ddagger_{298\text{K}} = 120 \pm 3 \text{ kJ mol}^{-1}$ . At suitably high temperatures, however, the resulting bis(alkynyl) **2** is formed under equilibrium and can be trapped out with CO or intercepted through irreversible reaction with H<sub>2</sub>, conferring overall exergonic processes. There is no reason to suspect that the kinetics or thermodynamics of the corresponding activation in **5** are significantly different. However, under the reaction conditions required to access the corresponding bis(alkynyl) derivative, Ar'<sup>2</sup>C<sub>4</sub>Ar' is preferentially displaced through low energy competing pathways, for instance by substitution with CO forming Rh<sup>I</sup>



**Scheme 4.** Qualitative energy profile illustrating why C(sp)–C(sp) bond oxidative addition of Ar'<sup>2</sup>C<sub>4</sub>Ar' and formation of **2** occurs in preference to substitution in **1**.



**Scheme 3.** Reaction of **1** with dihydrogen and related chemistry. Unless stated otherwise stated, reactions were performed in toluene/[D<sub>8</sub>]toluene under argon or hydrogen (1 atm). Ar' = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

carbonyl complex **6**. For **1** these competing pathways are blocked by steric constraints imposed by tight confinement of the diyne within the ring. For instance, in the case of the reaction of **1** with CO, a nominally putative intermediate in the associative substitution of Ar'C<sub>4</sub>Ar' by CO is formed reversibly, but dissociation of the diyne is ultimately prevented by buttressing with the tetradecamethylene strap. Similar arguments apply to the reaction of **1** with H<sub>2</sub>, although no adducts of **1** with this weaker ligand were detected.

More simply put, the mechanical bond does not fundamentally alter the capacity of **1** to undergo C(sp)-C(sp) bond oxidative addition of Ar'C<sub>4</sub>Ar', but instead enables this normally hidden reactivity to be accessed by disfavoring otherwise facile substitution of the substrate. Harnessing the mechanical bond in this manner not only represents an unprecedented strategy for probing the organometallic chemistry of C–C  $\sigma$ -bond activation reactions but showcases a novel practical application of interlocked molecules.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** C–C activation · macrocyclic ligands · pincer ligands · rhodium · rotaxanes

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- [16] The activation barrier for  $\pi$ -coordination shuttling in <sup>13</sup>C-**1** is equivalent, within experimental error, to that observed for **1**.

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- [18] Compared to **1**, acyclic **5** is characterized by a more ideal coordination geometry (e.g. C-Rh-alkyne = 178.68(8)°) and although the metal-alkyne contacts (2.072(4)/2.071(3), **1**; 2.080(2) Å, **5**) are not statistically different, spectroscopic data in solution and the solid state points toward slightly tighter alkyne binding (attenuated  $\pi$ -coordination shuttling,  $\Delta H^\ddagger = 80.0 \pm 0.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +17 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G^\ddagger_{298\text{K}} = 75 \pm 1 \text{ kJ mol}^{-1}$ ;  $\nu(\text{C}\equiv\text{C})_{\text{ATR}} = 1924$  (bound) and 2161 (free)  $\text{cm}^{-1}$ ).
- [19] No further reaction was apparent after heating the solution at 358 K for 24 h.
- [20] A. V. Polezhaev, S. A. Kuklin, D. M. Ivanov, P. V. Petrovskii, F. M. Dolgushin, M. G. Ezernitskaya, A. A. Koridze, *Russ. Chem. Bull.* **2009**, 58, 1847–1854.
- [21] Complex **1** can be quantitatively reformed by removal of CO from **4** in vacuo.
- [22] Deposition Numbers 1986033, 1986034, 1986035, and 1986036 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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