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Notes

Probing the Interactions of Transition-Metal Complexes Bound at the Ortho Position of Substituted Biphenyls

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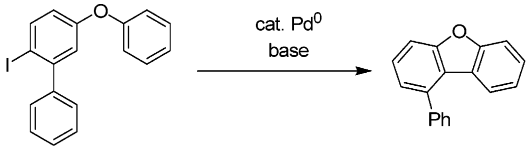
*Summary: (4,4′-dimethylbipyridyl)NiMe$_2$ was found to react thermally with 2-iodo-2′,4′,6′-trimethylbiphenyl (**6**) to produce a C−I insertion that is extremely distorted from square planarity, with the C−Ni−I plane intersecting the N−Ni−N plane by 33.4°. It was also found that [(dippe)RhCl]$_2$ reacts with **6** to produce an η^3-benzylic complex by way of a rhodium migration to the methylated ring of the biphenyl unit.*

Introduction

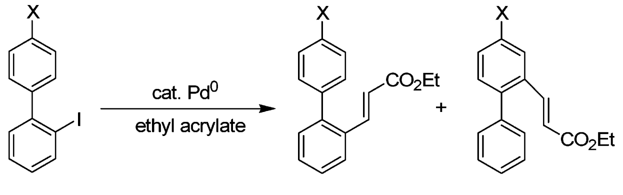
Biphenyls substituted at the position ortho to the aryl−aryl linkage are important synthetic precursors, as they have recently been used to prepare higher order polycycles. Larock, in particular, has developed palladium-catalyzed methods that can convert *o*-iodobiaryls such as **1** to a number of fused polycycles proceeding through oxidative addition of the C−I bond, followed by palladium migrations via C−H bond activation and subsequent C−C bond coupling to afford fused polycycles such as **2** (eq 1).[1] This palladium migration chemistry has also been observed during the palladium-catalyzed olefination of the asymmetrical *o*-iodobiphenyl **3** to afford the mixture of Heck products **4** and **5** (eq 2).[2] Of note was the unexpected migration of the palladium metal to the opposite ring of the biphenyl substrate. Clearly, the close proximity of aryl C−H bonds to transition metals bound in the 2-position of biaryls facilitates, and even promotes, a C−H bond activation step that normally would not readily occur.



1 **2**

(1)

We wondered what would happen if a transition metal, bound to the 2-position of a biphenyl substrate, did not have any readily available aryl C−H bonds for activation. If one could arrest the attachment of a metal to the 2-position of a biphenyl, more detailed information concerning the interactions of a metal with the organic ligand could be obtained. One obvious modification of a biphenyl substrate that would remove any proximal C−H bonds is the replacement of the 2′,6′-aryl hydrogens with methyl groups. Here we report the reactivity of 2-iodo-2′,4′,6′-trimethylbiphenyl (**6**) with a group 10 metal and describe some intimate details about the metal environment upon activation of the C−I bond of this sterically demanding substrate. Additionally we show that, depending on accessible oxidation states, metal migrations can still occur despite the absence of any available aryl C−H bonds.

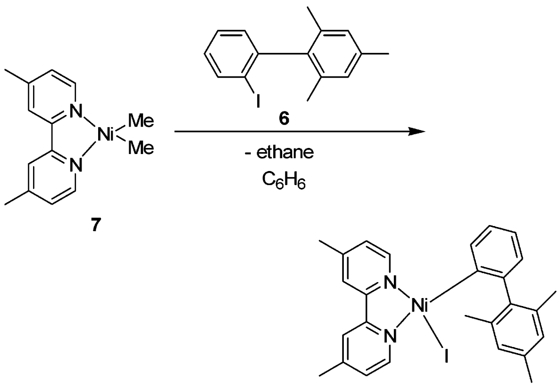


3 **4** **5**

(2)

Results and Discussion

Reaction of (bpy′)NiMe$_2$ (**7**; bpy′ = 4,4′-dimethylbipyridyl) with **6** for 2.5 h at 50 °C in benzene led to a complete color change of the solution from dark green to pink with formation of the C−I insertion product **8** (eq 3). Analysis of this new product by NMR spectros-



7 **8**

(3)

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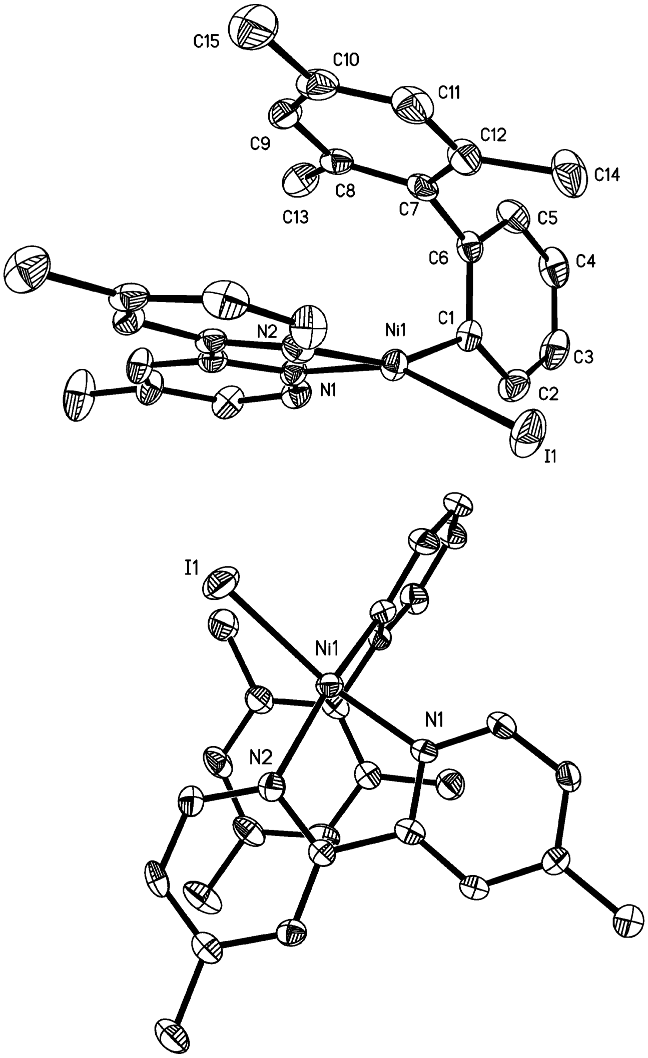

Figure 1. ORTEP diagrams of **8**, showing both a side-on view relative to the bpy′ ligand (top structure) and an overhead view (bottom structure). Ellipsoids are shown at the 50% level, with hydrogens omitted for clarity. Selected bond lengths (Å): I(1)−Ni(1) = 2.4793(6), Ni(1)−N(1) = 1.915(3), Ni(1)−N(2) = 1.962(3), Ni(1)−C(1) = 1.890(3). Selected bond angles (deg): N(1)−Ni(1)−N(2) = 82.8(1), N(1)−Ni(1)−C(1) = 94.6(1), N(1)−Ni(1)−I(1) = 154.29(7), N(2)−Ni(1)−C(1) = 158.8(1), N(2)−Ni(1)−I(1) = 99.2(1), C(1)−Ni(1)−I(1) = 92.2(1).

copy reveals that solutions of **8** can only be kept for a limited time, as the C−I insertion product decomposes readily into unidentified material. However, layering a cold THF solution of **8** with pentane at −30 °C afforded crystalline material fit for X-ray analysis, and the ORTEP diagrams are shown in Figure 1.

Compound **8** exhibits a number of interesting structural features in the solid state. The methylated ring of the biphenyl ligand lies almost parallel to the bpy′ ligand, with the two aromatic moieties assuming a novel "stacking"-type conformation (Figure 1). One can infer from the different views of the solid-state structure how a metal complex which has activated the C−I bond of an *o*-iodobiphenyl is in a particularly good position to activate the 2′- and 6′-positions of the biphenyl substrate. Simple rotation of the biaryl C−C bond is all that is needed to place any substituent on those positions in close proximity to the metal center.

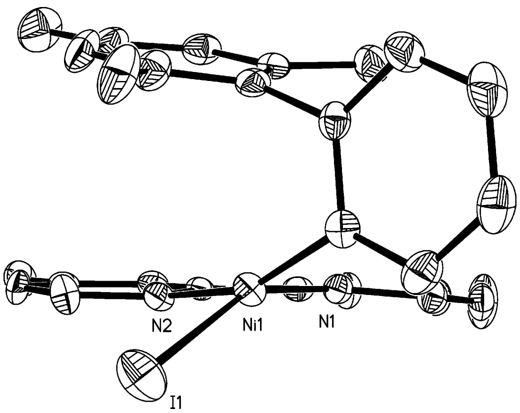

Figure 2. Alternate view of **8**, showing the distortion of the square plane around the nickel atom.

The structure of **8** is also interesting in terms of the distortion from square planarity that ensues upon C−I bond activation (Figure 2). The C1−Ni1−I1 plane intersects the N1−Ni1−N2 plane by 33.4°, which is to our knowledge the largest deviation from the square plane shown by a four-coordinate Ni^{II} complex containing a Ni−C bond. Tetrahedral Ni^{II} organometallic complexes are attractive synthetic targets, as high-spin methylnickel intermediates have been postulated in the A cluster of acetyl-coenzyme A synthase.[3−7] However, recent attempts at preparing high-spin Ni^{II} methyl complexes have proved unsuccessful.[8,9]

Interestingly, in the solution phase, complex **8** was found to adopt a symmetrical conformation. Three methyl resonances could be observed in the ^{1}H NMR spectrum of **8**, along with a total of eight broad signals for aromatic protons. Assuming that rotation of the aryl−aryl bond is restricted by geometrical constraints, these solution data are at least consistent with a tetrahedral arrangement of the ligands around nickel, with the methylated ring of the biphenyl symmetrically overlapping the bpy′ ligand. Although a tetrahedral Ni^{II} complex would formally be high spin and paramagnetic, it is not uncommon for paramagnetic nickel compounds to show broad, but distinguishable, resonances in the ^{1}H NMR spectra.[10] The solution data could also be consistent with equilibration of the iodide ligand to ether side of the metal via the fast equilibrium process outlined in eq 4. Such a process would produce symmetrical spectra similar to those seen for η^3-benzyl and allyl cation complexes of nickel[11,12] and would not require full rotation around the aryl−aryl bond. To investigate further the possibility of a high-spin, tetra-

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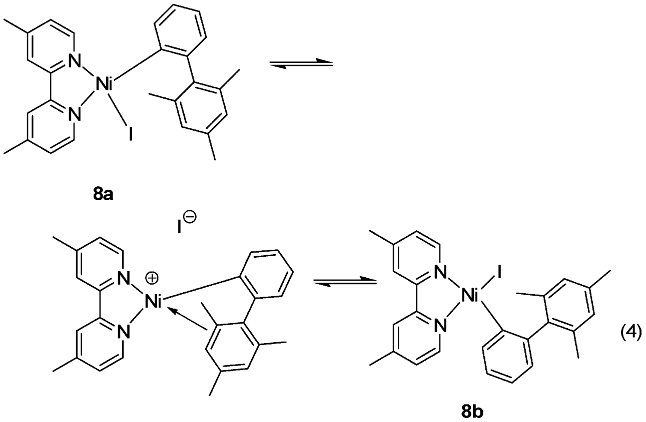
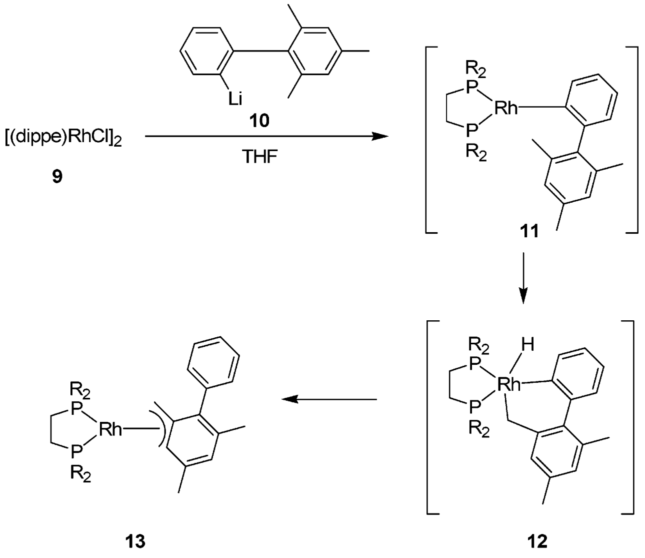


8a

8b

hedral nickel species, the magnetic susceptibility of **8** in benzene solution was determined by the Evans NMR method.[13] Large magnetic susceptibilities were found (consistently greater than $\mu_{\mathrm{eff}} = 3.0\ \mu_B$), but it is extremely difficult to interpret these data, as **8** is not completely stable in the solution phase (see above).

We have also found that, depending on the identity of the transition metal bound to the *o*-iodobiphenyl, rearrangements can still occur despite the absence of any available aryl C−H bonds. Upon reaction of [(dippe)RhCl]$_2$ (**9**; dippe = 1,2-bis-(diisopropylphosphino)ethane) with the lithiated biphenyl **10**, the expected product **11** is not observed (eq 5). Rather, complex **13**, which contains a rhodium atom bound to the methylated biphenyl ring, was the only apparent new product. A reasonable mechanism for this transformation is likely to involve activation of a benzylic C−H bond to produce the rhodium hydride **12**, followed by reductive elimination of the stronger aryl C−H bond to afford **13**. The migration process is extremely fast, as no hydride signals could be detected by ^{1}H NMR spectroscopy. Such a benzylic C−H bond activation process is similar to those recently reported by Catellani, who found that a constrained palladium complex can also activate ortho-substituted aryls, although an η^1- instead of an η^3-metalated product was formed.[14]



9

10

11

12

13

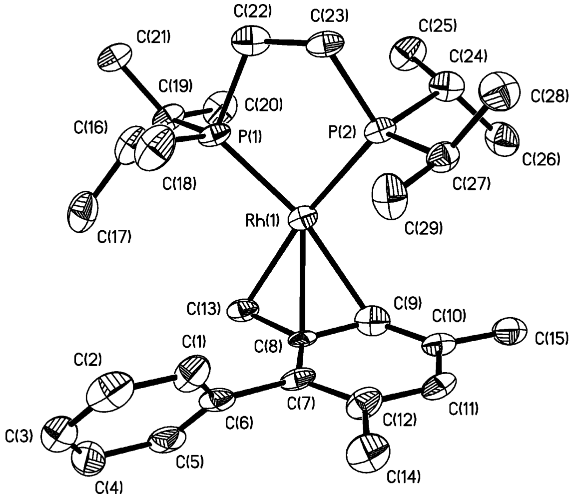


Figure 3. ORTEP diagram of **13**. Ellipsoids are shown at the 50% level. Hydrogens are omitted for clarity. Selected bond lengths (Å): Rh−P(1) = 2.210(4), Rh−P(2) = 2.234(3), Rh−C(8) = 2.21(1), Rh−C(9) = 2.35(2), Rh−C(13) = 2.17(1). C(8)−C(9) = 1.41(2), C(8)−C(13) = 1.43(2). Selected bond angles (deg): P(1)−Rh−P(2) = 86.8(1), P(1)−Rh−C(8) = 132.9(3), P(1)−Rh−C(9) = 166.3(3), P(1)−Rh−C(13) = 101.1(4), P(2)−Rh−C(8) = 133.2(3), P(2)−Rh−C(9) = 106.9(3), P(2)−Rh−C(13) = 171.2(4), C(8)−Rh−C(9) = 35.9(4), C(8)−Rh−C(13) = 38.0(5), C(9)−Rh−C(13) = 65.3(5).

Table 1. Crystal Parameters for Compounds 8 and 13

	8	**13**
chem formula	$C_{27}H_{27}IN_2Ni$	$C_{29}H_{47}P_2Rh$
formula wt	565.13	560.52
cryst dimens (mm)	0.20 × 0.25 × 0.30	0.10 × 0.20 × 0.25
color, habit	red, prism	orange, prism
cryst syst	triclinic	triclinic
wavelength, Å	0.710 70	0.710 70
μ (cm^{-1})	21.26	7.41
max−min transmissn	0.653−0.498	1.0000−0.4432
space group, *Z*	$P\bar{1}$, 2	$P\bar{1}$, 2
a, Å	8.854(13)	8.86(10)
b, Å	11.312(13)	8.97(17)
c, Å	12.50(2)	18.26(18)
α (deg)	78.76(12)	98.4(5)
β (deg)	78.19(12)	95.920(12)
γ (deg)	80.52(9)	101.5(3)
V, Å^3	1191.7(29)	1393.7(34)
ρ_{calcd}, g cm^{-1}	1.574	1.336
temp, °C	−100	−100
R indices ($I > 2\sigma(I)$)	0.0445, 0.0765	0.1384, 0.3014
R indices (all data)	0.0697, 0.0834	0.1751, 0.3214
goodness of fit	1.125	1.217
2θ range, deg	4.58−55.7	4.56−55.7
no. of data collected	8084	8335
no. of unique data	5477	5856
R_{int}	0.0235	0.1225

Compound **13** was also structurally characterized (Table 1), and although evidence for twinning was found, all atoms could be refined anisotropically. The ORTEP diagram of the new product is shown in Figure 3. X-ray analysis reveals that, upon migration to the benzylic carbon atom, the rhodium atom prefers to bind

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to the biphenyl substrate in an η^3 fashion, thereby increasing its electron count to 16 electrons. Interestingly, only one other η^3-benzylic complex of rhodium has been structurally characterized, namely (η^3-$CH_2C_6Me_6$)-Rh(P(O-*i*-Pr)$_3$)$_2$.[15] While this phosphite complex was prepared by addition of a hydride source to an arene complex of rhodium, we report here that **13** can be prepared directly from a C−H bond activation process.

Conclusions

A better picture is now emerging of the interactions of transition metals, bound to the 2-position of a biaryl unit, with substituents on the 2′- and 6′-positions of the adjacent ring. The steric interactions are large enough that metals with available oxidation states can activate benzylic C−H hydrogens, affording products in which the metal has migrated to the other arene ring. In the absence of readily available oxidation states, the inherent geometry of the biaryl ligand causes severe distortion of the ligand environment of the organometallic complex, due to the projection of the remaining arene ring back toward the metal center.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques or in a nitrogen-filled glovebox, unless otherwise noted. Solvents were distilled from Na/benzophenone or CaH_2. All reagents were used as received from commercial vendors unless otherwise noted. Aluminum oxide (activated, neutral, Brockmann I, ∼150 mesh) was dried at 200 °C under vacuum for 2 days prior to use. Elemental analyses were performed by Desert Analytics. ^{1}H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Bruker Avance 300 MHz spectrometer and referenced to residual proton solvent peaks. ^{31}P{^{1}H} NMR spectra were recorded on the Bruker Avance spectrometer operating at 121.44 MHz and referenced to an 85% phosphoric acid external standard set to 0 ppm. A Rigaku MSC Mercury/AFC8 diffractometer was used for X-ray structural determinations. **6**,[16] **7**,[17] and **9**[18,19] were prepared by previously published procedures.

Synthesis of (bpy′)Ni((η^1-2)-2′,4′,6′-trimethylbiphenyl)(I) (8). **7** (100 mg, 0.37 mmol) and 1 equiv of **6** were dissolved in 20 mL of benzene and heated to 50 °C for 2.5 h. The benzene was then removed on a vacuum line, and the residue was washed with pentane and filtered, leaving a burgundy solid. Yield: 32%. ^{1}H NMR (THF-d_8): δ 8.31 (br s, 2H), 7.83 (s, 2H), 7.56 (d, J = 6.30 Hz, 1H), 7.14 (br s, 2H), 6.83 (t, J = 6.69 Hz, 1H), 6.70 (t, J = 6.21 Hz, 1H), 6.55 (s, 2H), 6.47 (d, J = 6.74 Hz, 1H), 2.37 (s, 6H), 2.02 (s, 3H), 1.73 (s, 6H). Anal. Calcd for $C_{27}H_{27}IN_2Ni$: C, 57.05 (57.38); H, 5.02 (4.82).

Synthesis of (dippe)Rh(η^3-biphenyl) (13). Butyllithium (15.35 mL of a 1.02 M solution in hexanes) was added to a stirred solution of **6** (5.046 g, 15.6 mmol) in pentane at 0 °C. The solution was then warmed to room temperature and stirred for 3 h, during which time a white precipitate formed. The white precipitate was filtered, washed with pentane, and dried, affording **10** in 73.4% yield. Freshly prepared **10** (130 mg, 6.4 mmol) was then added to a stirred solution of **9** (246 mg, 0.31 mmol) in 50 mL of THF and stirred at room temperature for 1 h. The solvents were removed on a vacuum line, and the residue was extracted with pentane and filtered. The pentane was removed on a vacuum line, affording crude **13** (230 mg, 66%). The residue was dissolved in pentane and cooled to −35 °C overnight, leaving pure **13** as orange crystals (80 mg, 23% yield). ^{1}H NMR (C_6D_6): δ 7.67 (d, J = 7.58, 2H), 7.33−7.12 (m, 3H), 6.46 (s, 1H), 5.16 (s, 1H), 2.65 (m, 1H), 2.45 (s, 3H), 2.22−0.69 (m, 9H), 2.09 (s, 3H), 1.28 (dd, J = 7.29, 15.42, 3H), 0.59 (dd, J = 7.08, 15.42, 3H). ^{31}P{^{1}H} NMR (C_6D_6): δ 97.80 (dd, J_{Rh-P} = 242.5, J_{P-P} = 18.5 Hz), 89.09 (dd, J_{Rh-P} = 177.1, J_{P-P} = 19.6 Hz). Anal. Calcd for $C_{29}H_{47}P_2Rh$: C, 62.14 (61.75); H, 8.45 (8.51).

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Supporting Information Available: Crystal structure analysis reports, along with tables giving all X-ray data; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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