Organometallics **2005,** *24,* 4103−4105 4103

A New Cyclometalation Motif: Synthesis, Structure, and Reactivity of Palladacycles That Contain a Chiral Rhenium Fragment in the Backbone and Are Catalyst Precursors for Heck Reactions

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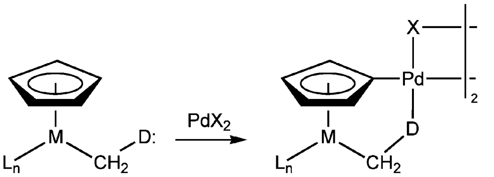
Received June 9, 2005

Summary: Reactions of (R)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]$^+X^-$, mild base, and Pd($OAc)_2$ yield the novel $Pd_3(OAc)_4$-based palladacycle (R,R)-(η^5-C_5H_4)Re(NO)(PPh_3)(μ-CH_2PPh_2)Pd(μ-OAc$)_2$Pd(μ-OAc$)_2$Pd(μ-PPh_2CH_2)Re(Ph_3P)(ON)(η^5-C_5H_4), which has been characterized crystallographically and elaborated to dimeric halide-bridged and monomeric palladacycles that are effective catalyst precursors for the Heck reaction.

Over the past few years, there has been an explosion of interest in palladacycle catalyst precursors, especially for carbon−carbon bond forming reactions.[1] Some of these have been particularly effective in high-turnover applications, often with aryl halide building blocks, and others have been rendered chiral and employed in enantioselective transformations. We have had a longstanding interest in catalysts that contain “spectator” metal fragments—i.e., ligand-based metals that do not directly participate in the catalytic cycle but whose steric and/or electronic properties may play important roles.[2−5] A variety of palladacycles that incorporate ferrocenyl or ruthenocenyl moieties have been reported,[6] but only a handful with other types of metallic units.[7,8]

We speculated that palladacycles might be generally available from half-sandwich complexes of the type **I** (eq i), which represent ubiquitous organometallic building blocks. There are a variety of donor-containing ligands −CH_2D: and/or −D: that might bind a palladium precursor (D: = halide, alkoxy, thioalkoxy, amido, phosphido, etc.) and facilitate subsequent metalation of the cyclopentadienyl ligand or a substituent thereof. Such complexes are easily rendered chiral, and there has been particular interest in introducing unusual new chirality motifs into palladacycles.[6,7] In this communication, we report the successful application of this strategy to enantiomerically pure “chiral-at-metal” rhenium complexes of the formula (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PR_2) and demonstrate the efficacy of the resulting palladacycles as catalyst precursors for Heck reactions.



I **II** (i)

The indefinitely stable phosphonium salt [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]$^+X^-$ ($\mathbf{1}^+X^-$) and *t*-BuOK react to give the corresponding neutral phosphorus donor (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2) (**2**).[3a,5a] Crystal structures establish, not surprisingly, retention of configuration at rhenium.[3a] As shown in Scheme 1, enantiopure (*R*)-$\mathbf{1}^+PF_6^-$, *t*-BuOK (1.2 equiv), and Pd($OAc)_2$ (1.5

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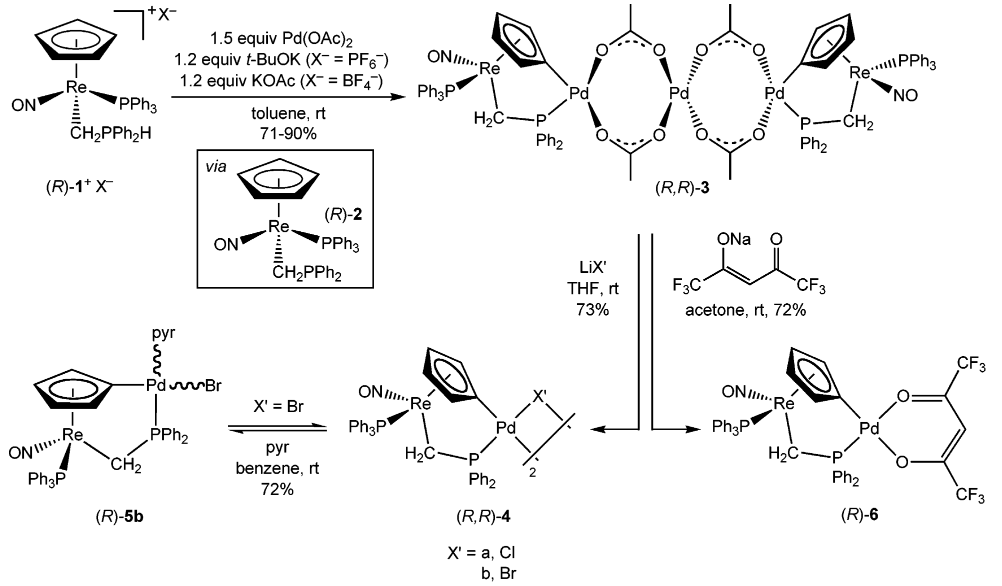
Scheme 1. Syntheses of Rhenium-Containing Palladacycles



equiv) were combined in toluene. Workup gave a palladacycle in high yield, as indicated by (1) ^{1}H and ^{13}C NMR spectra that showed characteristic patterns for a monosubstituted cyclopentadienyl ligand[3a,b] and (2) ^{1}H and ^{13}C NMR and IR evidence for acetate residues.[9] The same compound was obtained from (*R*)-**1**$^+$BF$_4^-$, the weaker base KOAc, and Pd(OAc)$_2$. However, microanalyses and certain mass spectral peaks were not consistent with the expected dimeric Re$_2$Pd$_2$(OAc)$_2$ structure. Thus, crystals of a toluene solvate were grown. As illustrated in Figure 1, X-ray data revealed an unusual S-shaped Pd$_3$(OAc)$_4$ core and the overall structure (*R*,*R*)-**3** (Scheme 1), corresponding to retention of configuration at rhenium.

Despite the very large number of molecules that have been palladated by Pd(OAc)$_2$, the central Pd$_3$(OAc)$_4$ moiety in (*R*,*R*)-**3** is extremely rare. To our knowledge, only two such trinuclear cores have been crystallographically characterized,[6k,10] although there is good support for others from spectroscopic data.[11] The three palladium atoms are approximately linear (∠ 177.46(2)°), with distances (2.9452(5) and 2.9330(5) Å) outside of bonding range.[12] As is evident in the bottom view in Figure 1, an idealized C_2 axis passes through the central palladium (perpendicular to the plane of the paper). In this perspective, the palladium-bound PPh$_2$ (and cyclopentadienyl) units appear syn.[13] Two other diastereomers with identical Pd$_3$(OAc)$_4$ conformations are possible (anti and syn′), but in solution only a single set of NMR signals was observed.

Since the central palladium in (*R*,*R*)-**3** might serve as a source of catalytically active Pd(OAc)$_2$, we sought to remove it. In one approach, the halide salts LiX′ were added (Scheme 1). Workups gave the Pd$_2$X′$_2$ complexes (*R*,*R*)-**4** (X′ = Cl (**a**), Br (**b**)) in 73% yields as mixtures of syn and anti isomers. These could be treated with a variety of neutral two-electron-donor ligands, such as pyridine, to give monopalladium complexes of the type (*R*)-**5b**. This complex crystallized in 72% yield; an X-ray analysis showed the pyridine and phosphorus ligands to be cis.[14] However, NMR spectra of solutions showed two isomers, as well as equilibrium concentrations of pyridine and (*R*,*R*)-**4b**. In another approach, (*R*,*R*)-**3** and the bidentate ligand sodium hexafluoroacetylacetonate (hfacac) were combined. Workup gave the monopalladium hfacac complex (*R*)-**6** in 72% yield.

The enantiomeric complex (*S*,*S*)-**4b** was evaluated as a catalyst precursor for Heck couplings of methyl acrylate and aryl bromides or iodides. As summarized in Scheme 2, reactions were carried out using 0.000 36–0.000 59 mol % loadings in DMF at 140 °C in the presence of NaOAc, (n-Bu)$_4$N$^+$Br$^-$, and an internal standard. After 48 h, GC analyses showed the aryl halides to be ≥92% consumed and 64–76% yields of the corresponding methyl cinnamate derivatives. These correspond to turnover numbers of 64 100–91 400. Reactions with (*R*)-**6** gave comparable data. However, in all cases TEM measurements showed the formation of colloidal palladium nanoparticles. This is frequently noted with "high turnover" Heck catalysts,[1,15] especially in recipes that involve (n-Bu)$_4$N$^+$Br$^-$,[15a] and suggests that the active catalyst is either non-molecular or a low-coordinate non-palladacyclic palladium(0) species.[16] The

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[9] All new compounds have been characterized by microanalysis, NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy, and mass spectrometry, as described in the Supporting Information.

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[13] Note that, with respect to the Pd–Pd–Pd axis, the PPh$_2$ unit on one terminus is anti to the cyclopentadienyl unit on the other.

[14] These data will be fully described in our full paper.

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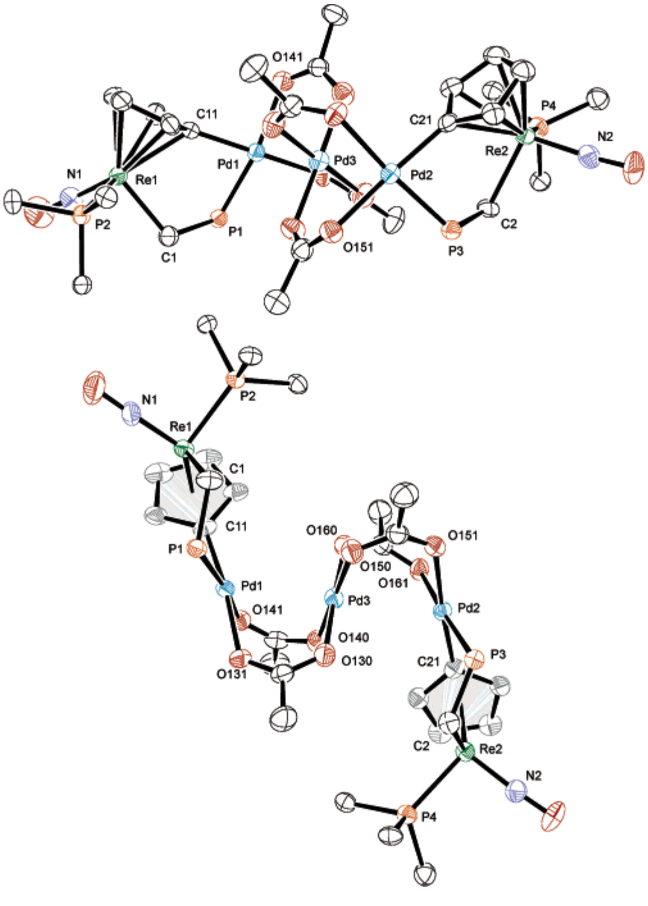
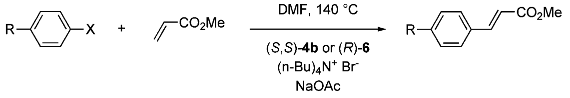


Figure 1. Structure of (R,R)-**3**$\cdot 2C_7H_8$ with solvate molecules and PPh_2 and para, meta, and ortho PPh_3 carbon atoms omitted. Key distances (Å): Pd1−Pd3, 2.9452(5); Pd2−Pd3, 2.9330(5); Pd1−C11, 1.983(5); Pd2−C21, 1.979(5); Pd1−P1, 2.1988(4); Pd2−P3, 2.1131(15); Pd1−O131, 2.126(4); Pd2−O151, 2.134(4); Pd1−O141, 2.133(4); Pd2−O161, 2.141(4); Re1−C1, 2.200(5); Re2−C2, 2.169(5); Re1−C11, 2.376(5); Re2−C21, 2.349(5). Key angles (deg): Pd1−Pd3−Pd2, 177.46(2); C11−Pd1−O131, 176.13(18); C21−Pd2−O151, 174.2(2); C11−Pd1−O141, 92.51(18); C21−Pd2−O161, 89.50(19); O131−Pd1−O141, 89.41(15); O151−Pd2−O161, 91.62(15); O131−Pd1−P1, 94.70(11); O151−Pd2−P3, 94.96(12); O141−Pd1−P1, 174.08(11); O161−Pd2−P3, 169.98(11); Pd1−C11−Re1, 127.5(2); Pd2−C21−Re2, 129.3(3); C1−Re1−C11, 81.92(19); C2−Re2−C21, 82.6(2); P1−C1−Re1, 108.8(3); P3−C2−Re2, 110.6(3); C1−P1−Pd1, 112.89(19); C2−P3−Pd2, 112.89(19); C11−Pd1−P1, 83.14(15); C21−Pd2−P3, 83.22(16).

complex (R,R)-**4b** was also evaluated in Heck reactions that operate at lower temperatures and yield chiral products,[17] but racemates were always obtained. Hence, there is no obvious effect or influence of the rhenium in any of our initial screening reactions.

Scheme 2. Heck Reactions Using Palladacycle Catalyst Precursors[a]



X	R	Catalyst, mmol	[ArX]/[Pd]	t (h)[(b)]	Conv[(c)]	Yield[(c)]	TON[(d)]
Br	CH_3CO	(S,S)-**4b**, 5.93×10^{-6}	84,400	48	92%	76%	64,100
I	CH_3	(S,S)-**4b**, 3.56×10^{-6}	140,600	48	100%	65%	91,400
I	H	(S,S)-**4b**, 4.74×10^{-6}	105,500	48	99%	64%	67,500
I	CH_3	(R)-**6**, 9.48×10^{-6}	105,500	30	86%	76%	80,200

[a] Conditions: ArX (1.000 mmol), methyl acrylate (ca. 2.22 mmol), NaOAc (1.4 mmol), $(n\text{-}Bu)_4N^+Br^-$ (0.2 mmol), DMF (5.00 mL). [b] After 24 h, the conversions were 42%, 86%, 72%, and 69%, respectively. [c] The conversion of the aryl halide and yield of the cinnamate product were determined by GC using bis(ethyleneglycol) dibutyl ether as internal standard. [d] Based upon the product yield and normalized for the number of palladium atoms in the catalyst.

In summary, we have established a simple route to a novel new class of palladacycles that contain metal cyclopentadienyl moieties in the backbone. One of these is fortuitously isolated with a rarely occurring $Pd_3(OAc)_4$ core. There is every reason to extrapolate that this methodology can be extended to a variety of other metals, donor groups, and ancillary ligands. These diversity elements could easily lead to thousands of catalysts, many of which would be chiral. Furthermore, other syntheses involving oxidative additions to halocyclopentadienyl ligands have also been established.[14,19] Although the new complexes in Scheme 1 are effective catalyst precursors for Heck reactions, the available data suggest that they act as sources of either palladium nanoparticles or achiral low-coordinate palladium(0) species. Nonetheless, there are many other types of reactions catalyzed by palladacycles,[1] several of which involve the formation of new stereocenters.[6d−f,h,i,k,7c−i,18] These are currently under active investigation. Also, the second metal in **I** might be engineered to have a labile set of ligands, such that *bi*metallic colloidal nanoparticles or non-molecular catalysts with unique reactivities would form under suitable conditions. Progress toward these ends will be described in future publications.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG, No. 300/4-2) and Johnson Matthey PMC (palladium loans) for support, Dr. K. Kromm for a discovery that paved the way for this chemistry,[14,19] and Dr. O. Delacroix for experimental assistance.

Supporting Information Available: Experimental procedures, characterization data[9] for all new compounds, and crystallographic data for (R,R)-**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0504708

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