[probably including the e_{1g} (d_{yz} and d_{zx}) virtual orbitals] are exposed outside the molecule as mentioned above. In fact, the stability of dibenzenechromium increases when methyl groups are introduced to the rings and protect the 3d-type orbitals against the attack of the reagents.

In conclusion, the wave function tail of metal orbitals in sandwich compounds can be effectively probed by PIES. Contrary to the general understanding that the 3d-type orbitals are significantly localized in the metal sphere, their tails have been found to be considerably exposed outside the molecule. This is especially true for the a_{1g} orbital, which has strong metal d_{z^2} character and is oriented normal to the rings. The present work has demonstrated that Penning ionization electron spectroscopy provides an insight into the reactivity of molecules.

New Living Polymerization of 1,2-Diisocyanoarenes via (Quinoxalinyl)palladium Complexes. Synthesis of Poly(2,3-quinoxaline)

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Polymerization of isocyanides catalyzed by transition-metal complexes involves a multiple successive insertion of isocyano groups into the carbon–metal linkage.[1] We have been studying a series of insertion reactions of isocyanides with an organometallic compound.[2] Recently, it was found that Grignard reagents promote new aromatizing oligomerization of 1,2-diisocyanoarene, which may arise from successive insertion of ortho isocyano groups on 1,2-diisocyanoarene into the carbon–magnesium bond.[3] However, the propagation of the oligomerization of 1,2-diisocyanoarene is rapidly terminated to give a mixture of quinoxaline oligomers from the monomer up to the hexamer, because of the instability of the propagating organomagnesium species. Now we report a new living polymerization of 1,2-diisocyanoarene giving poly(2,3-quinoxaline) via (quinoxalinyl)palladium complexes.[4]

1,2-Diisocyano-3,4,5,6-tetramethylbenzene (**1a**) reacted with *trans*-bromobis(dimethylphenylphosphine)methylpalladium(II) (**2**; 1.2 equiv) at room temperature in THF to afford *trans*-bromobis(dimethylphenylphosphine)(2,5,6,7,8-pentamethylquinoxalin-3-yl)palladium(II) (**3a**)[5] quantitatively. The (quinoxalinyl)palladium complex **3a** thus formed is stable in air and isolated by TLC on silica gel. A crystal suitable for X-ray structural analysis was obtained by recrystallization from dichloromethane–hexane and the crystal structure is shown in Figure 1.[5]

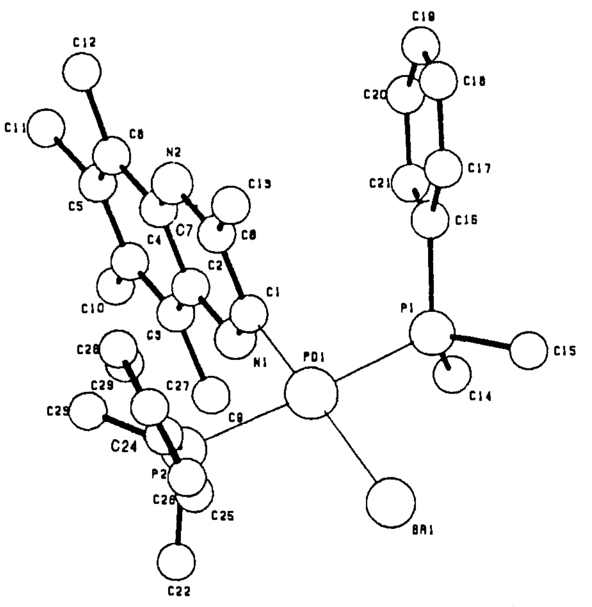
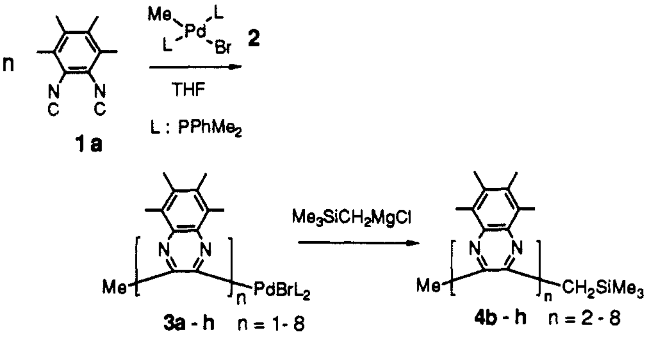


Figure 1. Structure of **3a**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (angstroms) and angles (degrees) are as follows: Pd-Br, 2.529 (1); Pd-P(1), 2.312 (2); Pd-P(2), 2.318 (2); Pd-C(1), 1.996 (6); Br-Pd-P(1), 94.3 (1); Br-Pd-C(1), 175.5 (2); C(1)-Pd-P(1), 85.5 (2).

Scheme I



Scheme II

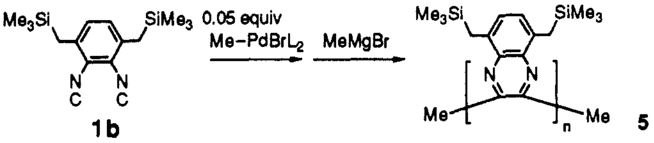


Table I. Reaction of **1a** with **2**

	yield, %							
1a/2	**4b**[a]	**4c**[b]	**4d**[c]	**4e**[d]	**4f**[e]	**4g**[f]	**4h**[g]	total
2	37	27	6	0	0	0	0	70
3	20	49	16	2	0	0	0	87
5	0	9	20	22	17	9	2	79
7	0	0	6	9	20	15	6	56

[a] $n = 2$. [b] $n = 3$. [c] $n = 4$. [d] $n = 5$. [e] $n = 6$. [f] $n = 7$. [g] $n = 8$.

Oligomerization of 1,2-diisocyanoarene **1a**, with the increased feeding ratio of **1a/2**, was propagated at reflux in THF to give a mixture of oligomeric (2,3-quinoxalinyl)palladium complexes (**3b–h**) in good total yields, which were transformed to [(trimethylsilyl)methyl]quinoxaline derivatives (**4b–h**)[6] for isolation by the reaction with [(trimethylsilyl)methyl]magnesium chloride. As seen from Table I, the higher oligomers were produced with

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(4) Arylnickel(II) complex, generated in situ from $NiCl_2(PMe_3)_2$ and Grignard reagent, also propagated a similar oligomerization of 1,2-diisocyanoarene.

(5) Spectral, analytical, and crystal data for **3a**: mp 190 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.48 (t, J_{P-H} = 3.6 Hz, 6 H), 1.52 (t, J_{P-H} = 3.6 Hz, 6 H), 2.29 (s, 3 H), 2.37 (s, 3 H), 2.41 (s, 3 H), 2.57 (s, 3 H), 2.68 (s, 3 H), 7.10–7.45 (m, 10 H); IR (KBr) 2916, 1530, 1438 cm^{-1}. Anal. Calcd for $C_{29}H_{37}BrN_2P_2Pd$: C, 52.62; H, 5.63; N, 4.23. Found: C, 52.55; H, 5.67; N, 4.24. Monoclinic, space group $P2_1/c$, a = 13.221 (2) Å, b = 8.499 (1) Å, c = 28.985 (5) Å, β = 112.57 (3)°, V = 3007.4 (9) Å^3, Z = 4, λ (Cu Kα) = 1.541 78 Å, μ = 80.2 cm^{-1}, R = 0.036, R_w = 0.046 including hydrogen atoms.

(6) UV data (CH_2Cl_2 solution). **4c**: λ_{max} (ϵ) 256 (35 900), 276 (31 800), 354 (18 800) nm. **4d**: λ_{max} (ϵ) 256 (59 200), 281 (55 800), 354 (35 100) nm.

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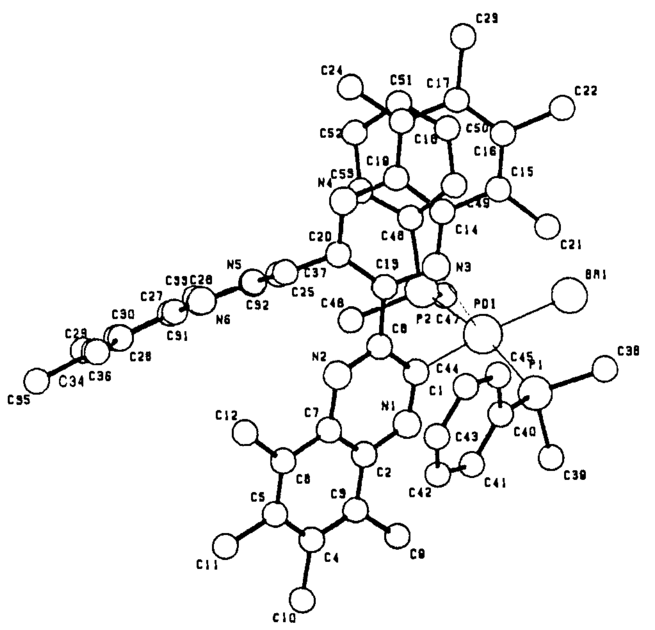

Figure 2. Structure of 3c. Two crystallographically independent molecules are present in the asymmetric unit; only one is shown. Selected interatomic distances (angstroms) and angles (degrees) are as follows: Pd-Br, 2.534 (1); Pd-P(1), 2.329 (2); Pd-P(2), 2.314 (2); Pd-N(3), 2.942 (5); Pd-C(1), 1.987 (5); Br-Pd-P(1), 92.0 (1); Br-Pd-C(1), 174.7 (1); Br-Pd-N(3), 115.1 (1); P(1)-Pd-N(3), 94.2 (1); C(1)-Pd-N(3), 69.8 (2).

the higher feeding ratio of **1a**/**2**. Although further polymerization also proceeded with the feeding ratio of over 7, insoluble polymers were produced.

The living polymerization mentioned above should be propagated via (quinoxalinyl)palladium complexes, which undergo successive insertion of ortho isocyano groups on 1,2-diisocyanoarene into their carbon-palladium linkage. Indeed, treatment of (biquinoxalinyl)palladium complex **3b** once isolated[7] with **1a** (2 equiv) resulted in the propagation to form a mixture of terquinoxaline (**3c**; 27%), quaterquinoxaline (**3d**; 28%), quinquequinoxaline (**3e**; 17%), and sexiquinoxaline (**3f**; 4%).[8] The structure of (terquinoxalinyl)palladium complex **3c**[7] was determined by X-ray crystallography (Figure 2).[9] Noteworthy is that the (terquinoxalinyl)palladium complex exists in distorted square-pyramidal five-coordination[10] in which nitrogen atom of the second quinoxaline unit coordinates to palladium atom at an axial position. It is of much interest that the reactive propagating species of living polymerization can be isolated and fully characterized.[4]

Finally, a soluble higher polymer with regular poly(2,3-quinoxaline) structure was successfully synthesized by use of 1,2-diisocyano-3,6-bis[(trimethylsilyl)methyl]benzene (**1b**); the reaction of **1b** with **2** (**1b**/**2** = 19) proceeded at reflux in THF to afford quinoxaline polymer **5** of $\bar{M}_n = 4830$ as determined by VPO in 65% isolated yield, which was soluble in common organic solvents such as chloroform and THF. **5**: yellow powder, UV (CH_2Cl_2 solution) λ_{max} 275 nm (ϵ 171 000). It should be noted that GPC using polystyrene as the standard indicated a very sharp distribution of molecular weight $\bar{M}_w/\bar{M}_n = 1.08$.

This method for controlled living polymerization offers a new entry to poly(heteroaromatics), which have attracted increasing attention owing to their interesting properties.

Supplementary Material Available: Experimental procedure for the reaction of **1a** with **2**, spectral and analytical data for **3b**, **3c**, and **4b–h**, and tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and bond angles for **3a** and **3c** (18 pages). Ordering information is given on any current masthead page.

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[7] (Biquinoxalinyl)- and (terquinoxalinyl)palladium complexes (**3b** and **3c**) were isolated by TLC (silica gel) of the reaction mixture of **1a** with **2** (**1a**/**2** and 2 and 3, respectively) followed by recrystallization from dichloromethane–hexane.

[8] Produced oligomers were isolated after conversion to **4c–f** by the reaction with [(trimethylsilyl)methyl]magnesium chloride (reflux in THF for 15 min).

[9] **3c**: triclinic, space group $P\bar{1}$, $a = 16.178$ (3) Å, $b = 24.714$ (5) Å, $c = 13.037$ (1) Å, $\alpha = 90.81$ (1)°, $\beta = 94.08$ (1)°, $\gamma = 106.77$ (2)°, $V = 4975$ (2) Å^3, $Z = 4$, λ (Cu Kα) = 1.541 78 Å, $\mu = 50.8$ cm^{-1}, $R = 0.048$, $R_w = 0.072$ excluding hydrogen atoms.

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Samarium-Catalyzed Intramolecular Tishchenko Reduction of β-Hydroxy Ketones. A Stereoselective Approach to the Synthesis of Differentiated Anti 1,3-Diol Monoesters

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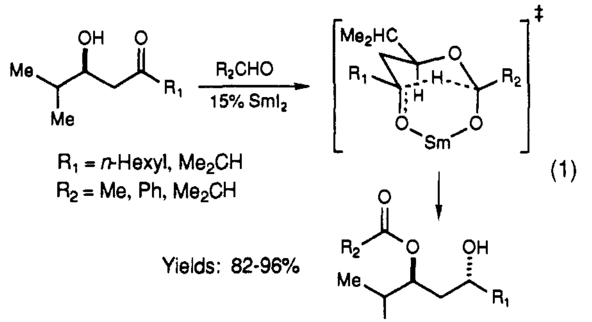
Those carbonyl and olefin addition reactions in which the reagent is "directed" through the active participation of functionality contained within the substrate provide the opportunity for both unique site selectivity and stereocontrol. Recent examples of directed hydrogenation,[1] hydride reduction,[2] and conjugate addition[3] complement the more traditional reactions in this class such as the Simmons–Smith reaction[4] and the Henbest and Sharpless allylic alcohol epoxidations.[5] In connection with our interest in the development of stereoselective reactions that may be employed in the synthesis of polyketide-derived natural products, we have evaluated a number of hydride reagents that might effect reduction of hydroxy ketones wherein the proximate heteroatom functionality strictly controls the facial selectivity of hydride delivery.[2b] We now report our findings on the samarium-catalyzed intramolecular Tishchenko reduction of β-hydroxy ketones (eq 1);[6,7] this transformation affords the corresponding



anti diol monoesters in high yield and with excellent levels of stereochemical control.[8]

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