from C1 of this ion produces $ROH_2^+$. Since the reactants in the second step cannot by joined by a covalent bond, beyond doubt $ROH_2^+$ formation occurs in an intermediate ion-neutral complex.

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## Spatial Distribution of 3d Electrons in Sandwich Compounds Studied by Penning Ionization Electron Spectroscopy: Ferrocene and Dibenzenechromium

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Electronic properties of sandwich compounds involving transition metals such as ferrocene have attracted considerable attention for many years. The nature of the chemical bond as well as the level ordering of the d states seem to be fairly well understood at present.[1] However, information on the spatial distribution of d electrons is rather limited, although it plays an important role in the stability of the complexes, the chemical reactions with other molecules, etc. In this communication we demonstrate that such information can be obtained directly by Penning ionization electron spectroscopy, in which the kinetic energy of electrons emitted by thermal collisions of rare-gas metastable atoms with target molecules is measured. For this purpose, we have taken up ferrocene ($(C_5H_5)_2Fe$) and dibenzenechromium ($(C_6H_6)_2Cr$) as samples, because they are closed-shell (diamagnetic) molecules with formal $d^6$ configurations and their ionization spectra are rather simple. Our data exhibit that the 3d-type orbitals of dibenzenechromium are considerably exposed to the outside of the molecule, while the corresponding orbitals of ferrocene are shielded by the rings effectively, as pointed out in a previous paper.[2]

Figure 1 shows Penning ionization electron spectra (PIES) of ferrocene and dibenzenechromium measured by a transmission-corrected electron spectrometer.[3-5] For reference, ultraviolet photoelectron spectra (UPS) of the two compounds are also shown in the figure. The highest lying two bands in both UPS have been attributed to emissions from the metal 3d-type $a_{1g}$ and $e_{2g}$ orbitals, while the next two bands are assigned to the $e_{1u}$ and $e_{1g}$ orbitals primarily composed of the ligand $\pi$.[6] Here, we used the notation of $D_{5d}$ symmetry (staggered conformation) for ferrocene,[7] in order to conform to the notation used in most previous works. The notation for dibenzenechromium is based on $D_{6h}$ symmetry.[8] $D_{5d}$ and $D_{6h}$ symmetries give the same notations for the orbitals mentioned above. As is seen in Figure 1, the four bands observed in the UPS also appear in the PIES. The characteristics of the PIES are summarized as follows:

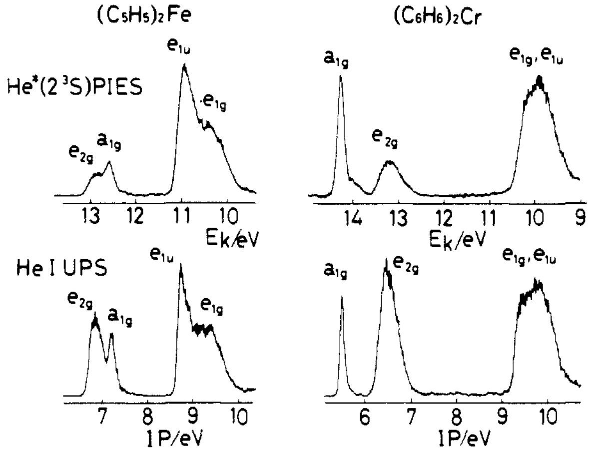

**Figure 1.** He*($2^3S$) PIES and He I UPS for ferrocene and dibenzenechromium. The kinetic energy scale for the PIES is shifted with respect to the UPS by the difference in the excitation energies, 21.22 − 19.82 = 1.40 (eV).

**Table I.** Relative Band Intensity in the PIES of Ferrocene and Dibenzenechromium

| MO | relative intensity[a] | |
|---|---|---|
| | ferrocene | dibenzenechromium |
| $e_{2g}$ ($d_{xy}$, $d_{x^2-y^2}$) | 16 | 42 |
| $a_{1g}$ ($d_{z^2}$) | 36 | 112 |
| $e_{1u}$ ($\pi$) | 100 | 100 |
| $e_{1g}$ ($\pi$) | | |

[a] Normalized relative band intensity corresponding to one orbital.

(i) As a common feature of the two compounds, in contrast to the UPS, the metal band due to the $a_{1g}$ orbital is much enhanced (more than twice) relative to that due to the $e_{2g}$ orbitals, taking the orbital degeneracy into account (see Table I).

(ii) With ferrocene, the intensity of the metal bands is much suppressed compared to that of the ligand bands. Such a marked suppression is not found in the case of dibenzenechromium.

Penning ionization is regarded as an electron-exchange process, in which an electron of a target molecule (M) fills the hole of a metastable atom (A*) and the excited electron is emitted to a continuum state simultaneously.[9] Since the transition rate for the electron transfer depends largely on the spatial overlap between the relevant occupied orbital of M and the empty orbital of A*, an orbital exposed outside the repulsive surface of the molecule M is expected to give a stronger band in PIES than does an orbital localized inside the molecule.[5] On the basis of this picture, the above result i indicates that the $a_{1g}$ (essentially $d_{z^2}$) orbitals are exposed further outside the molecules compared to the $e_{2g}$ (primarily $d_{xy}$ and $d_{x^2-y^2}$) orbitals. This feature can be understood easily from the fact that the vertical metal-to-ring distance in sandwich compounds (1.66 Å for ferrocene[7] and 1.62 Å for dibenzenechromium[8]) is rather short compared to the size of the ring (the distance between the center of ring and hydrogen is 2.34 Å for ferrocene and 2.51 Å for dibenzenechromium); the $3d_{z^2}$ orbital extending normal to the ring cannot be shielded by the orbitals of the rings so effectively as in the case of the $d_{xy}$ and $d_{x^2-y^2}$ orbitals. Next, result ii shows that the degree of exposure of the 3d-type orbitals outside the repulsive molecular surface is significantly larger for dibenzenechromium than for ferrocene. Since the Fe in ferrocene is formally dication, the contracted 3d orbitals are screened by the rings sufficiently in comparison with the 3d orbitals of formally neutral Cr in dibenzenechromium. An incomplete shielding effect for metal orbitals has also been observed in the case of benzene adsorbed parallel to transition-metal surfaces.[10]

It is known that dibenzenechromium is chemically unstable compared to ferrocene. This is mainly because the 3d-type orbitals

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(1) See, e.g.: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(2) Munakata, T.; Harada, Y.; Ohno, K.; Kuchitsu, K. *Chem. Phys. Lett.* **1981**, *84*, 6.

(3) Aoyama, M.; Masuda, S.; Ohno, K.; Harada, Y.; Mok, C. Y.; Huang, H. H.; Lee, S. Y. *J. Phys. Chem.* **1989**, *93*, 1800.

(4) Harada, Y.; Ohno, K.; Mutoh, H. *J. Chem. Phys.* **1983**, *79*, 3251.

(5) Ohno, K.; Mutoh, H.; Harada, Y. *J. Am. Chem. Soc.* **1983**, *105*, 4555.

(6) For ferrocene: Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; Van Tilborg, J.; Robbins, J.; Smart, J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327, and references therein. For dibenzene chromium: Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

(7) Ferrocene in the vapor phase is an eclipsed structure with $D_{5h}$ symmetry, while in the solid phase, it is a staggered structure with $D_{5d}$ symmetry (see: Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415).

(8) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41.

(9) Hotop, H.; Niehaus, A. *Z. Phys.* **1969**, *228*, 68.

(10) Masuda, S.; Aoyama, M.; Harada, Y., to be published.

[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]

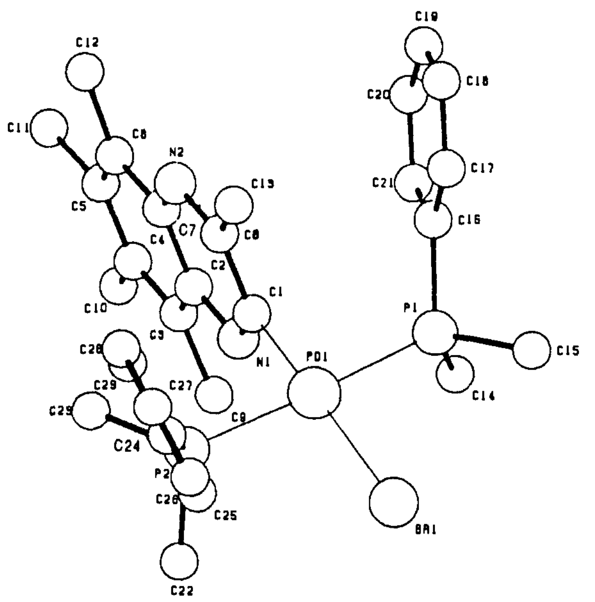
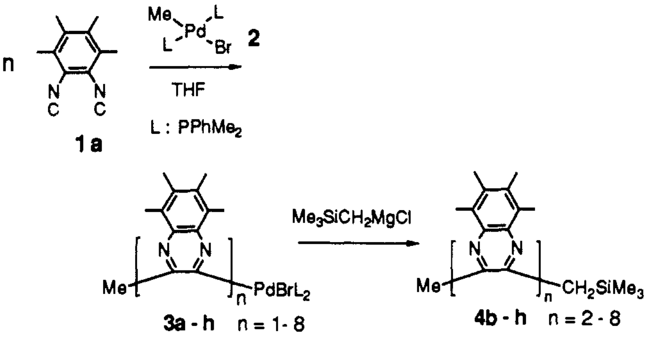


**Figure 1.** Structure of **3a**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (angstroms) and angles (degrees) are as follows: Pd–Br, 2.529 (1); Pd–P(1), 2.312 (2); Pd–P(2), 2.318 (2); Pd–C(1), 1.996 (6); Br–Pd–P(1), 94.3 (1); Br–Pd–C(1), 175.5 (2); C(1)–Pd–P(1), 85.5 (2).

**Scheme 1**



**Scheme II**

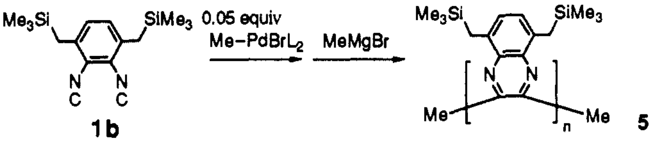


**Table 1.** Reaction of **1a** with **2**

| | 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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(1) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438.

(2) Murakami, M.; Ito, H.; Ito, Y. *J. Org. Chem.* **1988**, *53*, 4158. Murakami, M.; Kawano, T.; Ito, Y. *J. Am. Chem. Soc.* **1990**, *112*, 2437.

(3) Ito, Y.; Ihara, E.; Hirai, M.; Ohsaki, H.; Ohnishi, A.; Murakami, M. *J. Chem. Soc., Chem. Commun.* **1990**, 403.

(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; $^1H$ NMR ($CDCl_3$) $\delta$ 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, $\beta$ = 112.57 (3)°, $V$ = 3007.4 (9) Å$^3$, $Z$ = 4, $\lambda$ (Cu K$\alpha$) = 1.541 78 Å, $\mu$ = 80.2 $cm^{-1}$, $R$ = 0.036, $R_w$ = 0.046 including hydrogen atoms.

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

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