

proportional to the applied  $p(\text{O}_2)$ , thus providing a very useful tool for reporting the relative amount of oxygen present in the region of interest in a magnetic resonance image.

The relaxometric response may be modulated, according to the requirements of a given functional protocol, by introducing suitable substituents on the aromatic moieties of the porphyrin ring to control the thermodynamics and kinetics of the  $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$  switch. Moreover one may envisage several ways to attain longer  $\tau_{\text{R}}$  values—either by dealing with covalent macromolecular conjugates or by forming supramolecular adducts by interlocking of molecular components other than those used in this work.

### Experimental Section

The formation of  $[(\text{Mn}^{\text{II}} \text{ tpps})^{4-}]$  from  $[(\text{Mn}^{\text{III}} \text{ tpps})^{3-}]$  (Porphyrin Products, UT, USA) and  $\text{Na}_2\text{S}_2\text{O}_3$  was monitored by UV spectroscopy following the growth of the band at 428 nm and the disappearance of the band at 466 nm, typical for the +3 oxidation state. The binding affinity of the two complexes with poly- $\beta$ -CD was determined by measuring the water proton relaxation rates of a solution of the complex (about 0.2 mM) with increasing amounts of the poly- $\beta$ -CD substrate (0.2–14 mM). The data obtained were fitted with those calculated on the basis of the established theory of proton relaxation enhancement. The  $1/T_1$  NMRD curves were obtained on a fully automatic Field-Cycling Relaxometer (Stelar, Mede, PV, Italy) in the frequency range of 0.01–12 MHz. Data at higher frequencies were obtained on a Stelar Spin-Master Relaxometer (20 MHz) and on a Jeol EX-90 (90 MHz). The titrations with poly- $\beta$ -CD and the assessment of  $[(\text{Mn}^{\text{II}} \text{ tpps})^{4-}]$  as a  $\text{pO}_2$ -responsive agent were carried out at 20 MHz and 298 K.

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## Electrophilic Aromatic Substitution Reactions of a Metallabenzene: Nitration and Halogenation of the Osmabenzene $[\text{Os}\{\text{C}(\text{SMe})\text{CHCHCHCH}\}\text{I}(\text{CO})(\text{PPh}_3)_2]^{\ast\ast}$

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It was established at the outset, with the isolation of the first metallabenzenes,<sup>[1]</sup> that these compounds exhibit physical properties that are consistent with the presence of an aromatic ring system. The osmabenzene  $[\text{Os}(\text{CSCHCHCHCH})(\text{CO})(\text{PPh}_3)_2]$  displays ring planarity, equal Os–C distances intermediate between normal Os–C single and double bonds, C–C distances comparable to that found for benzene, and NMR chemical shifts appropriate for an aromatic system. The related iridabenzene  $[\text{Ir}(\text{CHCMeCHCMeCH})(\text{PET}_3)_3]$ ,<sup>[2]</sup> which has been extensively studied, shows similar physical properties.<sup>[3]</sup> A recently reported, but differently substituted iridabenzene,  $[\text{Ir}(\text{CPhCPhCHCHCH})(\text{CO})(\text{PPh}_3)_2]$ , again shows physical properties consistent with aromaticity.<sup>[4]</sup>

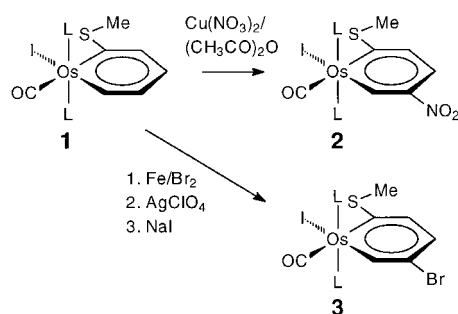
Despite the considerable weight of physical evidence pointing towards aromaticity for metallabenzenes, the reaction chemistry so far reported does not entirely reflect this. For example the iridabenzene  $[\text{Ir}(\text{CHCMeCHCMeCH})(\text{PET}_3)_3]$  has a propensity to undergo cycloaddition reactions rather than electrophilic substitutions.<sup>[3a]</sup> Other metallabenzenes are unstable with respect to rearrangement to cyclopentadienyl–metal complexes.<sup>[5]</sup> One hint of more conventional aromatic behavior is given by the formation of  $\eta^6$  complexes with other metal–ligand fragments, for example,  $[\{\eta^6\text{-CH=CMeCH=CMeCH-Ir}(\text{PET}_3)_3\}\text{Mo}(\text{CO})_3]$ .<sup>[6]</sup> Several related metallabenzene  $\eta^6$  complexes have also been described.<sup>[7]</sup>

Here we describe: 1) the first examples of electrophilic aromatic substitution of a metallabenzene, specifically both mononitration and monohalogenation of the osmabenzene  $[\text{Os}\{\text{C}(\text{SMe})\text{CHCHCHCH}\}\text{I}(\text{CO})(\text{PPh}_3)_2]$  (**1**) and 2) structure determinations of both the nitrated and brominated products, which reveal 3) the operation of a *para*-directing effect of the SMe ring substituent.

Treatment of the brown osmabenzene  $[\text{Os}(\text{CSCHCHCHCH})(\text{CO})(\text{PPh}_3)_2]$ ,<sup>[1, 8]</sup> with MeI produces the blue osmabenzene **1**, which bears an SMe substituent on the carbon atom adjacent to the osmium center (Scheme 1). The geometry of **1** has been confirmed by an X-ray crystal structure determination of its blue chloride analogue.<sup>[9]</sup> When **1** is subjected to the mild nitrating conditions offered by  $\text{Cu}(\text{NO}_3)_2/\text{acetic anhydride}$  and the crude reaction product

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Scheme 1. Electrophilic aromatic substitution reactions of **1** ( $\text{L}=\text{PPh}_3$ ).

purified by chromatography on silica gel, the blue-purple, mononitrated product,  $[\text{Os}\{\text{C}(\text{SMe})\text{CHCHC}(\text{NO}_2)\text{CH}\}\text{I}(\text{CO})(\text{PPh}_3)_2]$  (**2**), can be isolated in 5% yield (see Scheme 1). The presence of the nitro group is revealed by bands in the IR spectrum at 1526 and  $843\text{ cm}^{-1}$  (see *Experimental Section* for spectroscopic data for **1–3**). At the same time the frequency of the  $\tilde{\nu}(\text{CO})$  band increases from  $1939\text{ cm}^{-1}$  in **1** to  $1955\text{ cm}^{-1}$  in **2**. In the  $^1\text{H}$  NMR spectrum the resonances for the remaining three ring protons are consistent with the introduction of the nitro group *para* to the SMe group. This structural assignment is confirmed by the X-ray crystal structure of **2** (Figure 1).<sup>[10]</sup> Presumably the location of the nitro group is dictated by the directing effect of the SMe group as would be the case for a simple benzene derivative. The structure shows that both the nitro group and the SMe group lie in the plane of the osmabenzene ring.

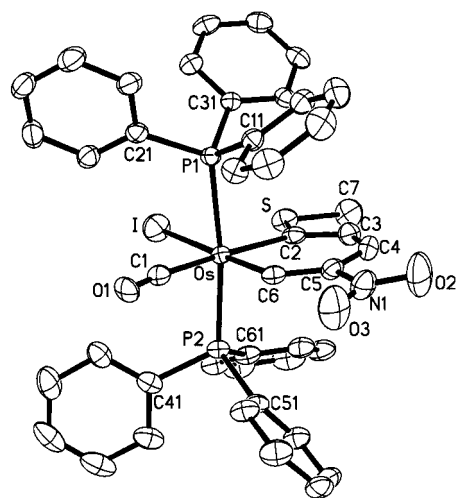


Figure 1. X-ray crystal structure of **2** (ORTEP). Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Os-C1 1.908(8), Os-C2 2.129(7), Os-C(6) 2.011(7), Os-P(1) 2.4005(16), Os-P(2) 2.4021(16), Os-I 2.8158(6), C2-C3 1.411(11), C3-C4 1.347(11), C4-C5 1.411(10), C5-C6 1.336(10), N1-C5 1.476(9), N1-O2 1.231(9), N1-O3 1.218(9), C2-S 1.702(7), C1-Os-C6 84.0(3), C2-Os-C6 87.1(3), C2-Os-I 90.9(2), C1-Os-I 98.1(2), P1-Os-P2 172.78(6).

In the same fashion, when **1** is treated with bromine/iron powder, bromination occurs, and the green complex  $[\text{Os}\{\text{C}(\text{SMe})\text{CHCHC}(\text{Br})\text{CH}\}\text{I}(\text{CO})(\text{PPh}_3)_2]$  (**3**) is obtained in an acceptable 40% yield (after chromatography). During this reaction some of the osmium-bound iodide is exchanged for bromide giving the mixture  $[\text{Os}\{\text{C}(\text{SMe})\text{CHCHC}(\text{Br})\text{CH}\}(\text{Br}/\text{I})(\text{CO})(\text{PPh}_3)_2]$ . The osmium-bound halide in this mixture is

labile and easily removed by the addition of silver perchlorate. Subsequent addition of excess sodium iodide gives pure **3**. Again the site of bromination is *para* to the SMe group as revealed by NMR spectroscopy (see below) and confirmed by X-ray crystal structure determination.<sup>[10]</sup> The molecular structure of **3** is shown in Figure 2. Chlorination of **1**, in the same ring position, has also been achieved through treatment of **1** with  $\text{PhICl}_2$  (20% yield, the product is blue-green).<sup>[9]</sup>

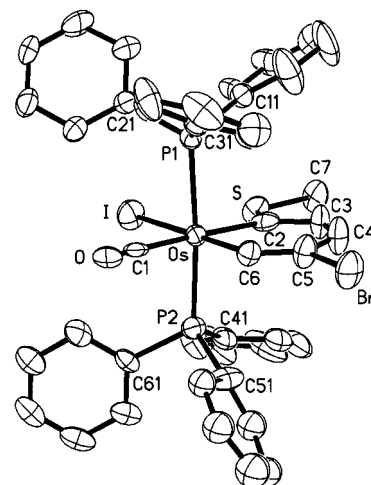


Figure 2. X-ray crystal structure of **3** (ORTEP). Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Os-C1 1.936(13), Os-C2 2.128(9), Os-C6 2.039(9), Os-P1 2.392(2), Os-P2 2.408(2), Os-I 2.8021(9), C2-C3 1.418(13), C3-C4 1.367(14), C4-C5 1.390(14), C5-C6 1.320(13), Br-C(5) 1.968(10), C2-S 1.702(10), C1-Os-C6 84.6(4), C2-Os-C6 87.2(4), C2-Os-I 91.7(3), C1-Os-I 96.6(3), P1-Os-P2 175.27(8).

These results indicate that osmabenzene **1** shows the defining chemical characteristic of aromaticity in undergoing the classical electrophilic aromatic substitution reactions of nitration and halogenation. Furthermore, normal directing (and presumably activating) substituent effects are apparent.

### Experimental Section

**1:**  $[\text{Os}\{\eta^5\text{-C}(\text{S})\text{CHCHCHCH}\}(\text{CO})(\text{PPh}_3)_2]$  (200 mg, 0.238 mmol) was dissolved in methyl iodide (25 mL) and the solution heated under reflux for 90 min. Addition of ethanol (20 mL) and removal of the methyl iodide under reduced pressure afforded teal-blue colored crystals of the title complex, which were recrystallized from dichloromethane/ethanol to give pure **1** (176 mg, 75%). M.p.  $175^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $24^\circ\text{C}$ , TMS) (the numbering scheme for the C and H atoms and the atoms of the metallacycles in **1–3** is shown in Figures 1 and 2):  $\delta = 1.55$  (s, 3H;  $\text{SCH}_3$ ), 6.21 ("t",  $^3J(\text{H,H}) = 8.5\text{ Hz}$ , 1H; H5), 6.60 (d,  $^3J(\text{H,H}) = 8.9\text{ Hz}$ , 1H; H3), 6.96 ("t"d,  $^3J(\text{H,H}) = 8.2$ ,  $^4J(\text{H,H}) = 1.8\text{ Hz}$ , 1H; H4), 12.74 (d,  $^3J(\text{H,H}) = 9.0\text{ Hz}$ , 1H; H6), 7.28–7.54 (m, 30H;  $\text{PPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ,  $24^\circ\text{C}$ , TMS):  $\delta = 23.20$  (s;  $\text{SCH}_3$ ), 121.62 (s; C3), 123.82 (s; C5), 145.85 (s; C4), 191.67 (t,  $^2J(\text{C,P}) = 11.1\text{ Hz}$ ; CO), 221.58 (t,  $^2J(\text{C,P}) = 6.3\text{ Hz}$ ; C6), 237.45 (t,  $^2J(\text{C,P}) = 9.1\text{ Hz}$ ; C2), 126.91 (t',  $^{1,11}2,4J(\text{C,P}) = 10.1\text{ Hz}$ ; *ortho*- $\text{PPh}_3$ ), 129.35 (s; *para*- $\text{PPh}_3$ ), 133.29 (t',  $^{1,3}J(\text{C,P}) = 53.3\text{ Hz}$ ; *ipso*- $\text{PPh}_3$ ), 134.74 (t',  $^{3,5}J(\text{C,P}) = 11.1\text{ Hz}$ ; *meta*- $\text{PPh}_3$ ); IR (Nujol):  $\tilde{\nu} = 1933$  (vs CO), 1523, 1384, 1347, 1246, 1220, 1146, 924, 840, 770,  $618\text{ cm}^{-1}$ ; positive-ion FAB-MS:  $m/z$ : 981.0623;  $\text{C}_{43}\text{H}_{37}\text{IOOsP}_2\text{S}$  requires 981.0622; elemental analysis calcd for  $\text{C}_{43}\text{H}_{37}\text{IOOsP}_2\text{S}$ : C 52.65, H 3.80; found: C 52.56, H 4.08.

**2:** Copper(II) nitrate (45.0 mg, 0.238 mmol) was dissolved in acetic anhydride (12 mL) under nitrogen and the solution cooled to  $0^\circ\text{C}$ . Complex **1** (200 mg, 0.238 mmol) was added, and the slurry was stirred at  $0^\circ\text{C}$  for 2 h. The ice bath was removed, and the green suspension was stirred for 1 h at room temperature. A mixture of sodium acetate (1 g) in

water (15 mL) and ice (40 g) was added, and the reaction mixture was stirred for a further 2 h during which time a black, oily solid separated out. The solution was removed by decantation, and the oily solid was dried in a vacuum desiccator. The dry residue was redissolved in dichloromethane (1 mL), placed on a silica gel column (2.5 cm  $\times$  1.5 cm), and eluted with dichloromethane. The fast-moving purple band was collected, ethanol was added, and the dichloromethane was removed under reduced pressure to yield green crystals. Recrystallization from dichloromethane/ethanol yielded pure **2** as purple crystals (12 mg, 5%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C, TMS):  $\delta$  = 1.84 (s, 3H;  $\text{SCH}_3$ ), 7.00 (d,  $^3J(\text{H,H})$  = 9.9 Hz, 1H; H3), 7.95 (dd,  $^3J(\text{H,H})$  = 9.8,  $^3J(\text{H,H})$  = 3.4 Hz, 1H; H4), 14.00 (m, 1H; H6), 7.20–7.56 (m, 30H;  $\text{PPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 24 °C, TMS):  $\delta$  = 24.70 (s;  $\text{SCH}_3$ ), 124.10 (s; C3), 138.90 (s; C4), 144.24 (s; C5), 212.54 (t,  $^2J(\text{C,P})$  = 10.6 Hz; CO), 222.69 (t,  $^2J(\text{C,P})$  = 6.0 Hz; C6), 127.32 (t',  $^{2,4}J(\text{C,P})$  = 9.1 Hz; *ortho*- $\text{PPh}_3$ ), 130.00 (s; *para*- $\text{PPh}_3$ ), 132.01 (t',  $^{1,3}J(\text{C,P})$  = 54.3 Hz; *ipso*- $\text{PPh}_3$ ), 134.41 (t',  $^{3,5}J(\text{C,P})$  = 10.0 Hz; *meta*- $\text{PPh}_3$ ); IR (Nujol):  $\tilde{\nu}$  = 1955 (vs CO), 1526 ( $\text{NO}_2$ ), 1299, 1276, 1237, 874, 843 ( $\text{NO}_2$ ), 745  $\text{cm}^{-1}$ ; positive-ion FAB-MS:  $m/z$ : 1024.0479;  $\text{C}_{43}\text{H}_{36}\text{INO}_3\text{OsP}_2\text{S}$  requires 1024.0473; elemental analysis calcd for  $\text{C}_{43}\text{H}_{36}\text{INO}_3\text{OsP}_2\text{S}$ : C 50.34, H 3.53, N 1.36, S 3.13; found: C 50.63, H 3.58, N 1.78, S 3.03.

**3**: Complex **1** (200 mg, 0.238 mmol) was dissolved in carbon tetrachloride (50 mL), and iron powder (1.0 mg, 0.018 mmol) was added. A solution of  $\text{Br}_2$  (12.2 mg, 0.238 mmol) in carbon tetrachloride (10 mL) was added dropwise to the blue solution. The reaction flask was heated on a water bath at 40 °C for 1 h. The carbon tetrachloride was removed in vacuo, and the green solid was dissolved in dichloromethane (1 mL) and placed on a silica gel column (2.5 cm  $\times$  1.5 cm). The blue-green fractions were collected, and  $\text{AgClO}_4$  (49.4 mg, 0.238 mmol) was added. The solution was stirred for 10 min, during which time a flocculant yellow solid appeared. The solution was then filtered through Celite, and NaI (71 mg, 0.48 mmol) in ethanol/water (10 mL/1 mL) was added. Removal of the dichloromethane, addition of ethanol (20 mL), and subsequent recrystallization of the crude product from dichloromethane/ethanol yielded dark green crystals of pure **3** (105 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 24 °C, TMS):  $\delta$  = 1.65 (s, 3H;  $\text{SCH}_3$ ), 6.79 (d,  $^3J(\text{H,H})$  = 9.5 Hz, 1H; H3), 7.15 (dd,  $^3J(\text{H,H})$  = 9.4,  $^3J(\text{H,H})$  = 3.0 Hz, 1H; H4), 12.61 (d,  $^3J(\text{H,H})$  = 2.9 Hz, 1H; H6), 7.20–7.52 (m, 30H;  $\text{PPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 24 °C, TMS):  $\delta$  = 20.28 (s;  $\text{SCH}_3$ ), 110.56 (s; C3), 126.14 (s; C4), 147.75 (s; C5), 190.73 (t,  $^2J(\text{C,P})$  = 11.1 Hz; CO), 210.81 (t,  $^2J(\text{C,P})$  = 5.5 Hz; C6), 240.31 (t,  $^2J(\text{C,P})$  = 9.1 Hz; C2), 127.36 (t',  $^{2,4}J(\text{C,P})$  = 10.1 Hz; *ortho*- $\text{PPh}_3$ ), 129.67 (s; *para*- $\text{PPh}_3$ ), 132.27 (t',  $^{1,3}J(\text{C,P})$  = 55.3 Hz; *ipso*- $\text{PPh}_3$ ), 134.39 (t',  $^{3,5}J(\text{C,P})$  = 10.1 Hz; *meta*- $\text{PPh}_3$ ); IR (Nujol):  $\tilde{\nu}$  = 1943 (vs CO), 1401, 1367, 1238, 1187, 922, 800, 668  $\text{cm}^{-1}$ ; positive-ion FAB-MS:  $m/z$ : 931.0697;  $\text{C}_{43}\text{H}_{36}\text{BrOOSp}_2\text{S}$  requires 931.0730 [ $\text{M}^+ - \text{I}$ ]; elemental analysis calcd for  $\text{C}_{43}\text{H}_{36}\text{BrIOOSp}_2\text{S} \cdot 0.5\text{CH}_2\text{Cl}_2$ : C 47.40, H 3.38; found: C 47.46, H 3.03.

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- [10] Data for the X-ray structure analyses: **2**: crystals from benzene/ethanol,  $\text{C}_{43}\text{H}_{36}\text{INO}_3\text{OsP}_2\text{S} \cdot 1.5\text{C}_6\text{H}_6$  ( $M_r$  = 1142.99); crystal dimensions 0.24  $\times$  0.24  $\times$  0.04 mm<sup>3</sup>; triclinic; space group  $P\bar{1}$ ;  $a$  = 12.2283(1),  $b$  = 13.7785(2),  $c$  = 14.1391(1) Å,  $\alpha$  = 80.144(1),  $\beta$  = 77.314(1),  $\gamma$  = 78.930(1)°,  $Z$  = 2,  $V$  = 2260.06(4) Å<sup>3</sup>,  $\rho_{\text{calcd}}$  = 1.680 g cm<sup>-3</sup>,  $T$  = 203 K;  $2\theta_{\text{max}}$  = 56°; 22095 total reflections of which 10023 were unique ( $R_{\text{int}}$  = 0.0268); Siemens SMART CCD diffractometer,  $\text{MoK}\alpha$  radiation ( $\lambda$  = 0.71073 Å); empirical absorption correction ( $\mu$  = 3.66 mm<sup>-1</sup>,  $T_{\text{min}}/T_{\text{max}}$  = 0.473/0.867). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares on  $F^2$ . The asymmetric unit contains one molecule of **2** and 1.5 molecules of benzene.  $R_1$  = 0.0477 for the 8702 observed data ( $I > 2\sigma(I)$ ) and  $wR_2$  = 0.1334 for all data; GOF( $F^2$ ) = 1.027. **3**: crystals from dichloromethane/ethanol,  $\text{C}_{43}\text{H}_{36}\text{BrIOOSp}_2\text{S}$  ( $M_r$  = 1059.73); crystal dimensions 0.21  $\times$  0.12  $\times$  0.08 mm<sup>3</sup>; orthorhombic; space group  $Pbca$ ;  $a$  = 14.211(2),  $b$  = 22.270(5),  $c$  = 24.315(3) Å,  $Z$  = 8,  $V$  = 7695(2) Å<sup>3</sup>,  $\rho_{\text{calcd}}$  = 1.829 g cm<sup>-3</sup>,  $T$  = 203 K;  $2\theta_{\text{max}}$  = 47°; 31267 total reflections of which 5529 were unique ( $R_{\text{int}}$  = 0.0795); Siemens SMART CCD diffractometer,  $\text{MoK}\alpha$  radiation ( $\lambda$  = 0.71073 Å); empirical absorption correction ( $\mu$  = 5.33 mm<sup>-1</sup>,  $T_{\text{min}}/T_{\text{max}}$  = 0.401/0.675). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares on  $F^2$ . The asymmetric unit contains a single molecule of **3**, in which one phenyl unit of one triphenylphosphane is disordered.  $R_1$  = 0.0437 for the 4190 observed data ( $I > 2\sigma(I)$ ) and  $wR_2$  = 0.1086 for all data; GOF( $F^2$ ) = 1.061. Programs used: SHELXS-97 (structure solution) and SHELXL-97 (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-133773 (**2**) and CCDC-133774 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [11] The denotation t' indicates that the signal has apparent multiplicity;  $^{nm}J(\text{C,P})$  is the sum of the two coupling constants  $^mJ(\text{C,P})$  and  $^nJ(\text{C,P})$  as explained in: S. M. Maddock, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1996**, *15*, 1793–1803.

## Highly Regio- and Stereoselective Cycloreductions of 1,6- and 1,7-Enynes Activated with a Carbonyl Functionality\*\*

Chang Ho Oh,\* Hyung Hoon Jung, Joo Sung Kim, and Seung Woo Cho

The cyclization of enynes or halodienes has been widely utilized in the synthesis of structurally complex natural and synthetic products.<sup>[1]</sup> Various 1,6- and 1,7-enynes, aided by suitable palladium catalysts, cycloisomerize to the corresponding dienes,<sup>[2]</sup> which could further serve as valuable

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