Table 1: Isoelectronic compounds with exchange of N for CH (A, B), structural isomers (A, C) with azadiene topology, and reagents to effect cyclometalation.

Substrate	Reagent
$ \begin{array}{c c} & & & \\ & & \\ & & \\ H & \\ $	[MnCH ₃ (CO) ₄] ^[3]
	[Fe(PMe ₃) ₄] [Fe(CH ₃) ₂ (PMe ₃) ₄] [CoCH ₃ (PMe ₃) ₄]
	[CoCH ₃ (PMe ₃) ₄]

conditions^[5] as well as their isoelectronic structural isomers having an azadiene topology, the 2-vinylpyridines (**C**, Table 1). The new, stable, and structurally characterized compounds containing N,C-metallacycles can be viewed as models for the organometallic intermediates in rutheniumand rhodium-catalyzed C–C coupling reactions between aromatic imines and olefins utilized in organic synthesis.^[6] In these reactions typically conducted in refluxing toluene the metalated species^[7] are not isolated but are converted into metal-free products in a catalytic process.

After simply combining the phenyl ketimines, benzaldimines, or 2-vinylpyridine with cobalt or iron complexes at -70 °C, we observed a color change indicating that the reaction was already occurring; for methyl complexes this was accompanied by evolution of gas (methane, GC). The mixture was warmed to 20 °C to give complete conversion and moderate to high yields of crystalline product (Table 2). Thus benzophenone imine was smoothly *ortho*-metalated with methyltetrakis(trimethylphosphane)cobalt [Eq. (1)].



The green crystals of **1** obtained from pentane decompose at 106 °C under argon; at 20 °C in air the crystal surface remains unchanged for at least 15 minutes. NMR spectra obtained from $[D_8]$ THF solutions are compatible with a trigonal-bipyramidal configuration around cobalt and a Caxial/N-equatorial coordination of the (2-iminobenzoyl)phenyl ligand. In the IR spectrum the ν (NH) band is observed with a hypsochromic shift of 45 cm⁻¹ indicating coordination through the N atom (Table 2).

The X-ray crystal structure of $\mathbf{1}^{[9]}$ confirms this configuration at cobalt. Bond lengths and angles in the molecule remain within the range of expected values. The sum of the internal bond angles of the chelate ring (542.6°) indicates little strain (planar five-membered ring: 540°). This is also reflected by the positions of the next-neighbor atoms at the metal

C–H Activation

Cyclometalation of Substrates Containing Imine and Pyridyl Anchoring Groups by Iron and Cobalt Complexes

Hans-Friedrich Klein,* Sebnem Camadanli, Robert Beck, Diana Leukel, and Ulrich Flörke

Cyclometalations transform barely activated or nonactivated C–H bonds of coordinated ligands into C–metal bonds. Metallacyclic species are known for almost all transition elements, and the majority of them contain five-membered rings.^[1] The first examples of cyclometalation were observed for azobenzene (**B**) with nickel, palladium, and platinum.^[2] Bruce et al. applied the reaction to Schiff bases of benzalde-hyde (**A**) and also described examples with manganese, rhenium, ruthenium, and rhodium (Table 1).^[3] If, in the series azobenzene, benzalaniline, and stilbene, N atoms are replaced by CH groups,^[4] then elevated temperatures are required for cyclometalation to occur. The reaction with benzalaniline must be run in THF or toluene at reflux, and stilbene does not react.

We have recently been able to effect cyclometalation reactions for the first time at basic cobalt and iron centers by using imine and pyridyl anchoring groups. Phenyl ketimines and benzaldimines react smoothly under particularly mild

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Communications



an octahedral coordination environment made up of three PMe_3 groups in meridional positions, the N,C-chelate ligand, and a hydrido ligand *trans* to the imine donor of the chelate. The methyliron compound **3** shows the same configuration in solution, except that the Fe–H group of **5** is replaced by a Fe–CH₃ group. Compounds **5** and **4** are isoelectronic by the analogy of Co and Fe-H.

Combining 2-vinylpyridine with methyltetrakis(trimethylphosphane)cobalt in THF resulted in evolution of gas and a color change from orange–red to green. According to Equation (3) the metallacyclic complex **6** formed.

(3)



Dark green crystals of **6** were grown from pentane at -20 °C; their surface planes reflect incident daylight as red light. At 78 °C under argon these dichroitic properties were lost, and thermal decomposition commenced. When air was admitted, the crystals rapidly deliquesced and underwent oxidative decomposition already at 20 °C. Both the NMR spectra in [D₈]THF and the crystal structure of **6**^[12] (Figure 2)



Figure 2. X-ray crystal structure of *2.* Selected distances [Å] and angles [°]: Co1–C7 1.913(2), Co1–N1 2.006(2), Co1–P1 2.1526(7), Co1–P2 2.2030(7), Co1–P3 2.1575(7), C6–C7 1.337(3); N1-Co1-C7 80.5(1), P2-Co1-C7 175.50(8).

show molecular complex entities in which the C-donor function is axial and the N-donor function is equatorial. The chelate and the metal center form a planar five-membered ring with a typical bite angle at the cobalt atom (N1-Co-C7 80.5(1)°).

The IR spectra of by-products give no evidence for isomers. Also, in the course of the analogous formation of 7 neither of the two aromatic C–H groups available for the



Figure 1. X-ray crystal structure of **1**. Selected distances [Å] and angles [°]: Co1–N1 1.882(5), Co1–C12 1.959(6), Co1–P1 2.2178(18), Co1–P2 2.1858(19), Co1–P3 2.189(2), N1–C10 1.337(8); N1-Co1-C12 80.6(2), C12-Co1-P1 168.15(19), C10-N1-Co1 121.5(4).

center, which show no gross deviation from ideal trigonalbipyramid coordination (Figure 1).

When an equimolar mixture of tetrakis(trimethylphosphane)iron and (2,2-dimethyl-1-phenyl)propylidenimine^[10] in pentane was warmed from -70 °C to 20 °C, the initial orange mixture turned dark red. Through oxidative addition the hydridoiron(II) complex **5** formed [Eq. (2)].



Violet crystals of **5** are stable up to 118 °C under argon. According to NMR spectra in $[D_8]$ THF^[11] the iron center has

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formation of six-membered metallacycles were activated in competition with the vinyl group.

This result demonstrates that in structural isomers containing a 1,4-interchanged azadiene topology (Table 1) activation occurs at the formally interchanged C-H group, which may be aromatic or vinylic. Furthermore these findings are in accord with the notion^[13] that the N-donor function is coordinated first, followed by activation and regiospecific cleavage of the most suitable ligand C-H bond. The M-H function thus formed either remains in the final product, as observed after reaction at the iron(0) center, or when there is an adjacent M-CH₃ unit, it is eliminated as methane as in all the other cyclometalation reactions described here. As the metals retain their low oxidation states in the products and since the effects of donor ligands are similar before and after reaction, except for the chelate effect, it should be possible to perform a second C-H activation. Subsequent elimination accompanied by C-C coupling would facilitate a catalytic reaction mode. Experiments with this aim are currently under way.

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removed in vacuo, and the residue was extracted with fresh pentane over a glass-sinter disc (G3). When the solution was cooled, crystals formed. The solution was decanted off, and the crystals were washed with cold pentane and dried in vacuo to afford analytically pure materials **1–7** (Table 2).

- [9] Crystal data for 1: $C_{22}H_{37}CoNP_3$, $M_r = 467.4$; crystal size: $0.20 \times 0.25 \times 0.35$ mm, orthorhombic, space group $Pna2_1$, a = 16.815(4), b = 9.473(3), c = 15.676(5) Å, V = 2497.0(13) Å³, Z = 4, $\rho_{calcd} = 1.243$ gcm⁻³, F(000) = 922; 2974 reflections with $2.84^{\circ} < 2\theta < 49.98^{\circ}$, Stoe-Stadi-4 diffractometer, $Mo_{K\alpha}$ radiation, no absorption correction, graphite monochromator, structure solution using Patterson and Fourier methods, refinement from 2974 independent reflections ($R_{int} = 0.0925$) for 244 parameters based on F^2 with SHELXL97, R = 0.0460, wR2 = 0.1073 (all data). Max./min. residual electron densities 0.593/-0.373 e Å⁻³. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were set at calculated positions.
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- [12] a) Crystal data for 6 ($C_{16}H_{33}CoNP_3$): $M_r = 391.3$; crystal size: $0.40 \times 0.35 \times 0.25$ mm, monoclinic, space group $P2_1/c$, a =14.753(2), b = 14.528(2), c = 9.9920(14) Å, $\beta = 102.975(2)^{\circ}$, V =2086.9(5) Å³, Z=4, $\rho_{\text{calcd}} = 1.245 \text{ g cm}^{-3}$, F(000) = 832; 23679 reflections with 2.84° < 2θ < 56.78°, Bruker AXS SMART APEX CCD^[14] diffractometer, Mo_{Ka} radiation (μ = 1.047 mm⁻¹), graphite monochromator, semiempirical absorption correction using equivalent reflections (SADABS^[14]). Structure solution using direct methods,^[14] refinement^[14] from 5022 independent reflections ($R_{int} = 0.050$) for 199 parameters based on F^2 , $R1 (I > 2\sigma(I)) = 0.038$, wR2 (all data) = 0.092. Max./ min. residual electron densities 0.49/-0.22 e Å⁻³. All non-hydrogen atoms were refined anisotropically, hydrogen atoms with riding model at idealized positions and isotropic parameters $U_{iso}(H) = 1.2 U_{eq}(C)$ or $1.5 U_{eq}(-CH_3)$. b) CCDC-240668 and -239924 (1 and 6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ ccdc.cam.ac.uk).
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