

Communications to the Editor

An Electronically Unsaturated Trinickel Complex Containing Triply Bridging Benzyne and 2,2'-Biphenyl Groups

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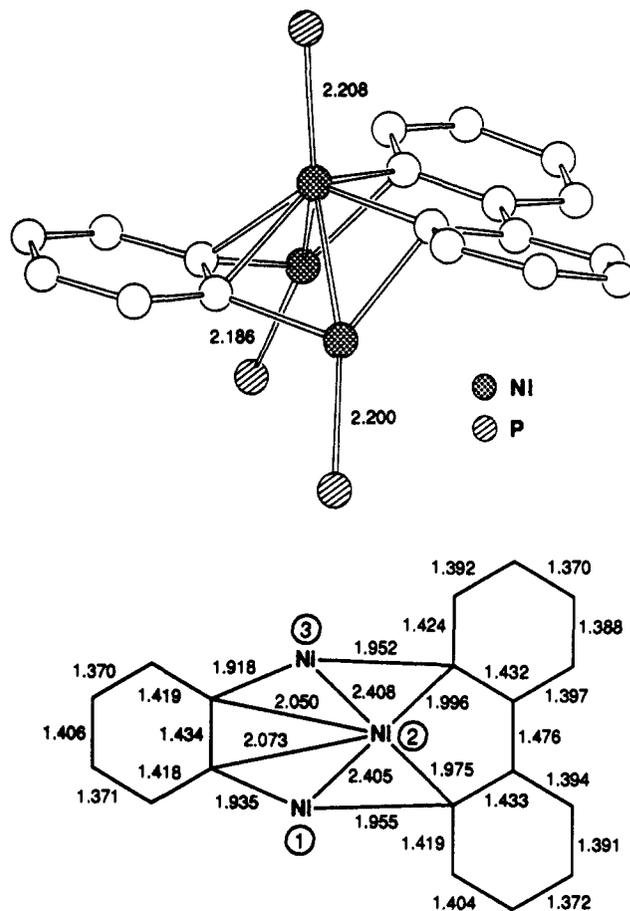
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Benzyne (*o*-phenylene, C₆H₄) and its derivatives can act as η² ligands donating between two and four electrons in monomeric transition-metal complexes,¹ e.g., TaCp*Me₃(η²-C₆H₄),^{2,3} ZrCp₂(η²-C₆H₄)(PMe₃),⁴ Re(η²-3-MeC₆H₃)(η¹-2-MeC₆H₄)₂L₂ (L = PMe₃, PMe₂Ph),⁵ Ru(η²-C₆H₄)(PMe₃)₄,⁶ and Ni(η²-C₆H₄)(Cy₂PCH₂CH₂PCy₂) (1).⁷ They can also behave as bridging ligands in polynuclear metal complexes and are often generated when aromatic derivatives are heated with Os₃(CO)₁₂ or Ru₃(CO)₁₂. A common structural type contains a four-electron donor C₆H₄ group lying over a triangle of osmium or ruthenium atoms, e.g., Os₃(CO)₉(μ-H)₂(μ₃-C₆H₄) (2),⁸ M₃(CO)₇(μ-PPh₂)₂(μ₃-C₆H₄) [M = Os (3),⁹ Ru (4)],¹⁰ and Os₃(CO)₉(μ-H)(μ-AsMe₂)(μ₃-C₆H₄) (5).¹¹ In the course of preparing analogues of 1 containing monodentate tertiary phosphines, we have isolated and structurally characterized a trinickel complex containing both μ₃-C₆H₄ and a novel bridging 2,2'-biphenyl group, C₆H₄-C₆H₄.

Reduction of NiCl(2-C₆H₄)(P-*i*-Pr₃)₂ (6)¹² with 1% sodium amalgam in THF gives two products in variable proportions that can be separated by fractional crystallization from diethyl ether. The main product, isolated in 30–50% yield, is the yellow, crystalline, η² benzyne complex Ni(η²-C₆H₄)(P-*i*-Pr₃)₂ (7), identified by comparison of its spectroscopic properties¹³ with those of



$$\sigma_{\text{Ni-Ni}} \sigma_{\text{Ni-P}} < 0.001 \text{ \AA}; \sigma_{\text{Ni-C}} 0.002 \text{ \AA}; \sigma_{\text{C-C}} 0.003-0.004 \text{ \AA}$$

Figure 1.

complex 1. The minor product, isolated in 4–30% yield, is a black, crystalline solid (8) that slowly decomposes in solution giving triphenylene. In the aromatic region, the ¹H NMR spectrum of 8 shows six peaks of equal intensity and the ¹³C{¹H} NMR spectrum shows nine resonances, consistent with the presence of two different C₆H₄ environments in a 2:1 ratio.¹⁴ The appearance of an AX₂ pattern in the ³¹P{¹H} NMR spectrum and the resonances of the CH(CH₃)₂ groups in the ¹H and ¹³C NMR spectra indicate that there are two P-*i*-Pr₃ ligands of one type and one of another.

These features are accommodated by the molecular structure shown in Figure 1, which has been determined by single-crystal X-ray analysis.¹⁵ It consists of a near-right-angled isosceles

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(2) Abbreviations: Cp* = η⁵-C₅Me₅; Cy = cyclohexyl, C₆H₁₁; COD = 1,5-cyclooctadiene; tmeda = tetramethyl-1,2-ethylenediamine.

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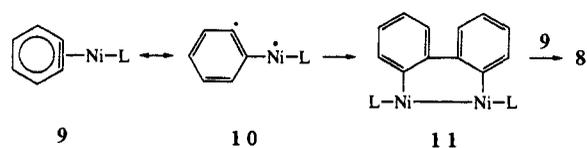
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(12) Made by addition of *o*-dichlorobenzene to a mixture of Ni(COD)₂ and trisopropylphosphine in a 1:2 mole ratio.

(13) ¹H NMR (THF-*d*₆) δ 7.17 (m), 6.72 (m) (AA'BB'), 2.32 (m, CH-(CH₂)₂), 1.30 (dd, J_{HH} = 7.5 Hz, J_{PH} = 12.5 Hz, CH₃); ¹³C{¹H} NMR (THF-*d*₆) δ 141.4 (qn, ²J_{PC} + ²J_{PC} = 33.7 Hz, benzyne C), 126.6 (t, J_{PC} + J_{PC} = 7.5 Hz), 123.4 (t, J_{PC} + J_{PC} = 15 Hz) (aromatic CH), 27.6 (filled in doublet, ¹J_{PC} + ³J_{PC} = 17.6 Hz, PCC), 20.8 (s, PCC); ³¹P{¹H} NMR (THF-*d*₆) δ 56.4 (s); IR (KBr) 1598 cm⁻¹ (s, ν(C≡C)).

(14) ¹H NMR (THF-*d*₆) δ 8.19 (d), 7.53 (m), 7.30 (d), 6.86 (t), 6.69 (t), 6.16 (dd) (C₆H₄), 1.84 (m, PCH), 1.49 (m, PCH) (ca. 2:1 ratio), 1.02 (dt, J_{HH} = 7.7 Hz, ³J_{PH} + ⁵J_{PH} = 12.5 Hz, CH₃), 0.76 (dd, J_{HH} = 7.0 Hz, J_{PH} = 12.1 Hz, CH₃) (ca. 2:1 ratio); ¹³C{¹H} NMR (THF-*d*₆) δ 171.7 (d, J_{PC} = 29 Hz), 160.6, 149.4 (aromatic C), 150.1, 126.9, 122.6, 122.1, 121.3, 118.9 (aromatic CH), 24.5–23.5 (m, PCC), 21.5–19.5 (m, PCC); ³¹P{¹H} NMR (THF-*d*₆) δ 39.3 (d, 2 P), 20.1 (t, 1 P) (J_{PP} = 37 Hz); ³¹P{¹H} NMR (C₆D₆) δ 39.0 (d, 2 P), 18.7 (t, 1 P) (J_{PP} = 36 Hz).

Scheme 1



triangle of nickel atoms each bearing one triisopropylphosphine ligand [Ni(1)–Ni(2) = 2.405 (1) Å, Ni(2)–Ni(3) = 2.408 (1) Å, Ni(1)–Ni(2)–Ni(3) = 90.81 (2)°]. The triangle is bridged by a C₆H₄ unit on one face and a 2,2'-biphenyl (C₆H₄–C₆H₄) unit on the other; the Ni₃(μ₃-C₆H₄)(μ₃-C₆H₄–C₆H₄) core exhibits almost exact mirror symmetry. The four-electron-donor benzyne unit is σ-bonded to Ni(1) and Ni(3), and π-bonded to Ni(2), the geometry being like that found in complexes 2–5. In contrast, the 2- and 2'-carbon atoms of the C₆H₄–C₆H₄ unit are σ-bonded to Ni(2) and bound orthogonally to Ni(1) and Ni(3), respectively. The four Ni–C distances to the C₆H₄–C₆H₄ unit are in the range 1.95–2.00 Å, which is similar to that observed for the compounds [Ni(C₆H₅)₂(CH₂ = CH₂)₂Na₄(THF)₅]¹⁶ and C₆H₅(Na·OEt)₂–[Ni(C₆H₅)₂]₂(N₂)NaLi₆(OEt)₄·OEt₂,¹⁷ in which the phenyl groups bridge nickel and sodium atoms, but greater than that found in the η¹-phenylnickel(II) complexes Ni(η-C₅H₅)(C₆H₅)(PPh₃) [1.904 (7) Å]¹⁸ and [Ni(C₆H₅)[N(CH₂CH₂AsPh₂)₃]]BPh₄ [1.87 (2) Å].¹⁹ Although the 2- and 2'-carbon atoms in 8 are each nearly equidistant from the bridged pair of nickel atoms, the σ-bonded nickel atom Ni(2) is within 0.1 Å of the C₆H₄–C₆H₄ ring plane, whereas nickel atoms Ni(1) and Ni(3) are 1.75 and 1.72 Å, respectively, below the plane. Thus, the interactions of the 2- and 2'-carbon atoms with the nickel atoms differ from the more usual three-center, two-electron bonds found in the 2,2'-biphenyllithium compound (C₆H₄–C₆H₄)Li₂(tmeda)₂,²⁰ and in other μ-aryls and μ-alkyls of main group and transition elements, e.g., Al₂(μ-C₆H₅)₂(C₆H₅)₄,²¹ Os₃(CO)₈(μ₂-PPh₂)(μ₂-PPhC₆H₄)(μ₂-C₆H₅),^{9a} Pt₃(PPh₃)₂(μ₂-PPh₂)₃(μ₂-C₆H₅),²² and Ni₂(μ₂-CH₃)₂(η³-1,3-dimethylallyl)₂.²³

Complex 8 can be classified as a 44e cluster if we assume that μ₃-C₆H₄ and μ₃-C₆H₄–C₆H₄ donate four electrons each to the three nickel atoms and if we exclude Ni–Ni bonding electrons. It is therefore related to the unsaturated clusters of the nickel triad such as Pt₃(CN-*t*-Bu)₆ (42e),²⁴ Pt₃(CO)₃(PCy₃)₃ (42e),²⁵ and Pt₃(CO)₃(PCy₃)₄ (44e),²⁶ which, however, differ from 8 in having equilateral triangles. The only other compound in which a μ₃-alkyne is attached to an isosceles triangle of nickel atoms is the

electronically saturated 48e-complex Ni₃(CO)₃(μ₃-CF₃C₂CF₃)(μ₃-η⁸-C₈H₈).²⁷

The benzyne and 2,2'-biphenyl ligands display well-defined intra-ring bond length (and bond angle) inequalities (Figure 1). The pattern in the benzyne ring resembles that observed in 4. However, the distance between the metal-bound carbon atoms [1.434 (3) Å] and also the average length of the remaining C–C bonds (1.403 Å) in the μ₃-C₆H₄ ring each significantly exceed the corresponding values in 4 (1.40 and 1.38 Å, respectively). This agrees with the idea that the electronic unsaturation of 8 reduces the π-orbital population of its *o*-phenylene group relative to that in the 48e complex 4.

Since 8 is not formed from 7 under the reaction conditions, we suggest that the first step is dissociation of one of the bulky *P*-*i*-Pr₃ ligands from 6. Two-electron reduction of the resulting three-coordinate nickel(II) complex could give a 14e benzyne–nickel(0) fragment Ni(C₆H₄)(*P*-*i*-Pr₃) (9), which could be regarded as the nickel(I) complex of a phenyl radical (10) (Scheme 1). Such a compound could be expected to dimerize to the 2,2'-biphenylnickel(I) species 11, which could react with more 9 to give the trimeric compound 8. A somewhat similar stepwise sequence in which free arynes react with organolithium compounds has been invoked to account for the formation of triphenylenes from the thermal decomposition of 2-halophenyl derivatives of lithium or magnesium,²⁸ and from the reaction of lithium metal with *o*-diiodobenzene or *o*-bromiodobenzene.²⁹ Experiments to test the proposed sequence and to prepare related clusters containing other alkynes and metals are in progress.

Supplementary Material Available: Tables of crystal data, non-hydrogen atom position and thermal parameters, and bond lengths and angles (9 pages); listing of observed and calculated structure factors for 8 (30 pages). Ordering information is given on any current masthead page.

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A Heterogeneous "Ligand-Accelerated" Reaction: Enantioselective Hydrogenation of Ethyl Pyruvate Catalyzed by Cinchona-Modified Pt/Al₂O₃ Catalysts

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Enantioselective hydrogenation reactions are a topic current interest.¹ While there is a growing understanding of the mechanism of homogeneously catalyzed reactions,² less is known about chiral heterogeneous catalysts.³ One such enantioselective catalytic system, Pt/Al₂O₃ modified with cinchona alkaloids, is able to hydrogenate α-keto esters with optical yields approaching 90%.^{4–7} It was noted that modification leads to a marked increase in reaction rate,⁶ suggesting a mode of action that has recently

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(15) Crystallography: Philips PW1100/20 diffractometer, Mo Kα radiation (λ = 0.7107 Å, graphite crystal monochromator), 4 deg min⁻¹ 2θ, 2 × 5 s backgrounds at extremes, T = 164 K. Black, metallic crystals from diethyl ether; C₄₅H₇₅P₃Ni₃; triclinic, space group P1, a = 19.467 (3), b = 11.116 (2), c = 10.542 (2) Å; α = 78.22 (1), β = 84.78 (1), γ = 85.44 (1)°; M_r = 885.15; ρ_{calcd} = 1.32 g cm⁻³; Z = 2; μ = 13.9 cm⁻¹. Specimen crystal dimensions 0.45 × 0.23 × 0.14 mm., maximum/minimum transmission = 0.84/0.76. A total of 12384 measured reflections (±h±k±l, 5 < 2θ < 45°), 5169 unique observed reflections (I ≥ 3σ). Structure solution by direct methods (DIRDIF); refinement by full-matrix least-squares on F²; non-hydrogen atoms anisotropic, hydrogen atoms located by calculation, reflection weights (σ_F² + 0.0005F²)⁻¹; 460 refined parameters, R = 0.022, R_w = 0.033, GOF = 1.23; maximum shift/error = 0.16, maximum/minimum excursions in final difference map +0.27/–0.25 e Å⁻³.

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