Organometallics **1996,** *15,* 2855−2857 2855

Chain Extension and C−C Bond Formation on C_4 Polycarbon Ligands: Novel Chemistry of *σ*-*π*-Butadiynyl Complexes with Carbene Sources

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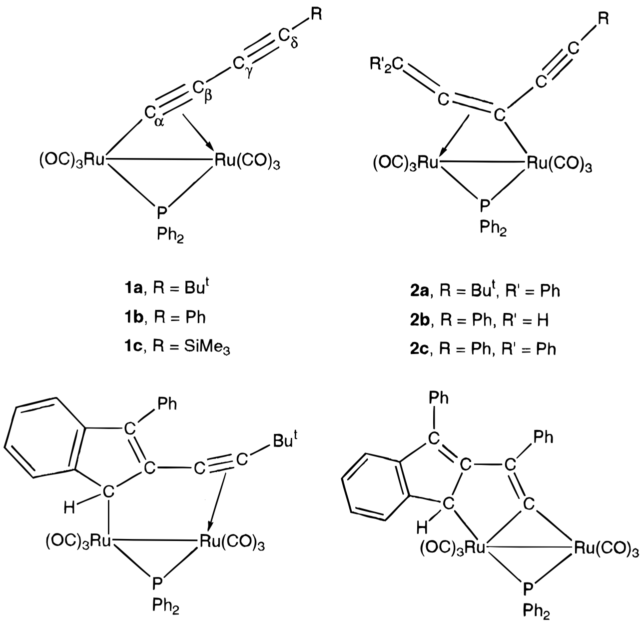
Received March 25, 1996[⊗]

*Summary: Reaction of $Ru_2(CO)_6(\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}CC{\equiv}CR)(\mu\text{-}PPh_2)$ (**1a**, R = Bu^t; **1b**, R = Ph) with the carbene precursors R'_2CN_2 (R′ = H, Ph) affords the 1-ynyl−allenyl complexes $Ru_2(CO)_6(\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}C(C{\equiv}CR){=}C{=}CR'_2)(\mu\text{-}PPh_2)$ (**2a**, R = Bu^t, R′ = Ph; **2b**, R = Ph, R′ = H; **2c**, R = R′ = Ph) via attack of the carbene group at C_α of the butadiynyl ligand. In the case of Ph_2CN_2, carbene addition also occurs at C_β to give the η^1-indenyl derivatives $Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^2\text{-}CH(C_6H_4)C(Ph){=}CC{\equiv}CBu^t\}(\mu\text{-}PPh_2)$ (**3**) or $Ru_2(CO)_6\{\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)(C_6H_4)CH\}(\mu\text{-}PPh_2)$ (**4**) via two carbon−carbon bond-forming processes. The molecular structures of **2a**, **3**, and **4** have been determined by X-ray crystallography.*

Ynyl and polyynyl ligands ($-C{\equiv}CR$, $-(C{\equiv}C)_x-$) are unrivaled in their ability to link metal centers into linear chains via M−C(sp) bonds, and considerable effort is being devoted to the synthesis of rodlike materials and wires from these building blocks.[1] However, the full potential of the $-(C{\equiv}C){-}R$ group lies in the exploitation of *π*-interactions to construct two- and three-dimensional multimetallic arrays. Yet despite an extensive organometallic chemistry for monoalkynyl ligands,[2] the behavior of polycarbon ligands such as butadiynyls ($-C{\equiv}CC{\equiv}CR$) or higher polyynyls $-(C{\equiv}C)_x$-R with extended sp unsaturation at polynuclear centers has only just begun to attract attention.[3] We have recently described a route to the first series of μ-$\eta^1{:}\eta^2$-butadiynyl complexes $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}CC{\equiv}CR')(\mu\text{-}PPh_2)$ (R = Bu^t, **1a**; R = Ph, **1b**; R = $SiMe_3$, **1c**)[3b,4] which possess one *π*-coordinated and one pendant triple bond. In this communication we report evidence for novel chemistry for these complexes. Reactions with carbene sources result in exclusive attack at the coordinated ynyl multiple bond, leading to new C_5 ynyl−allenyl ligands via chain extension and $\eta^1{:}\eta^2$-indenylacetylenes via intramolecular cyclization. These results herald a rich and diverse chemistry for multimetal bound polyynyl ligands.

Chart 1



1a, R = Bu^t
1b, R = Ph
1c, R = $SiMe_3$

2a, R = Bu^t, R′ = Ph
2b, R = Ph, R′ = H
2c, R = Ph, R′ = Ph

3

4

Treatment of the μ-$\eta^1{:}\eta^2{}_{\alpha,\beta}$-butadiynyl complex **1b** with diazomethane under CO at −10 °C in hexane afforded, after thin-layer chromatography on silica, yellow **2b** (R = Ph, R′ = H, 35%)[5] (Chart 1). Under similar conditions **1a** did not react with CH_2N_2 but **1a** and **1b** on reaction with diphenyldiazomethane Ph_2CN_2 (80 °C, toluene) gave analogues **2a** (R = Bu^t, R′ = Ph; 10%) and **2c** (R = R′ = Ph; 22%)[6] as well as a second isomeric product **3**[7] (R = Bu^t; 22%) and **4**[8] (R = Ph; 15%), respectively. Separation of **2a** and **3**, **2c** and **4** was

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[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1996.

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(5) Spectroscopic data for **2b**: IR (C_6H_{14}) ν(CO)/cm^{-1} 2077 s, 2051 vs, 2016 s, 2000 m, 1984 w; ^1H NMR ($CDCl_3$) δ 7.54−7.01 (m, 15H, Ph), 4.23 (d, J_{HH} = 1.9 Hz, 1H, CH_2), 3.93 (d, J_{HH} = 1.9 Hz, 1H, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 127.6 (s). Anal. Calcd for $C_{29}H_{17}O_6PRu_2$: C, 50.15; H, 2.47. Found: C, 50.56; H, 2.87.

S0276-7333(96)00221-X CCC: $12.00

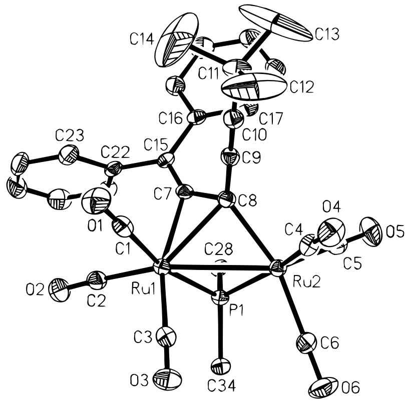

Figure 1. Molecular structure of $[Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C(C{\equiv}CBu^t){=}C{=}CPh_2)(\mu\text{-}PPh_2)]$ (**2a**) with the non-hydrogen atom labeling scheme. For clarity, only the *ipso* carbons of the *P*-phenyl rings are drawn. Important bond lengths (Å) and angles (deg) not mentioned in the text are as follows: Ru(1)−Ru(2) = 2.825(1), Ru(1)−C(7) = 2.170(3), Ru(1)−C(8) = 2.297(3), C(8)−C(9) = 1.438(5), C(10)−C(11) = 1.475(5); C(8)−C(7)−C(15) = 144.6(3), C(7)−C(8)−C(9) = 114.3(3), C(8)−C(9)−C(10) = 178.9(4), Ru(1)−P(1)−Ru(2) = 73.6(1)°.

accomplished by thin-layer chromatography. Although spectroscopic data for **2a**−**c** were indicative of coordinated allenyl and free alkyne functionalities, single-crystal X-ray analyses of **2a**,[9] **3**,[10] and **4**[11] were necessary to fully establish the structures of the products.

The most striking feature of the structure of **2a** (Figure 1) is the presence of a five-carbon chain derived from the original $\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CC{\equiv}CBu^t$ ligand by adding a $:CPh_2$ fragment at C_α.[12] The polyunsaturated penta-1-yne-3,4-dien-3-yl (or ynyl−allenyl) ligand is attached to Ru(2) via a σ-bond to C(8) (Ru(2)−C(8) = 2.095(3) Å), the β-carbon of the original $\mu\text{-}\eta^1{:}\eta^2\text{-}C_\alpha{\equiv}C_\beta C_\gamma{\equiv}C_\delta Bu^t$ group, and to Ru(1) via an η^2-interaction with the new C(7)−C(8) allenyl double bond (C(7)−C(8) = 1.411(5) Å). The outer C(7)−C(15) double bond (C(7)−C(15) = 1.323(5) Å) of the C(8)−C(7)−C(15) allenyl ligand is uncoordinated, as is the alkyne functionality C(9)−C(10) (1.191(5) Å) attached to C(8). The overall coordination of the new allenyl ligand closely resembles that in $Ru_2(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}C(Ph){=}C{=}CPh_2)(\mu\text{-}PPh_2)$[13] and is reflected in the similarity of the $C_\alpha-C_\beta-C_\gamma$ angles (144.0(4) *vs* 144.6(3)° in **2a**). Complexes **2b** and **2c** are assigned similar ynyl−allenyl structures on the basis of close correspondence of spectroscopic features to **2a**. The conversion of **1a**,**b** to **2a**,**c** is the first example of a C_4 to C_5 chain extension at a $-C{\equiv}CC{\equiv}CR$ ligand and represents a viable route to a new class of substituted allenyl complexes. Although not synthesized via chain extension, other molecules with a cumulated C_5 linkage $L_nM{=}C{=}C{=}C{=}C{=}CR_2$, have recently been prepared[14] via OR′ elimination from the pentadiynyl complexes $L_nMC{\equiv}CC{\equiv}C\text{-}CR_2OR'$.

An X-ray analysis of **3**, the second CPh_2 addition product of **1a**, revealed attack of the carbene group at a C_β position, as shown in Figure 2. In this case the *ortho* carbon atom of one of the phenyl rings has become attached to C_α of the original butadiynyl ligand, the latter also becoming bonded to the liberated *ortho* hydrogen atom to generate an η^1-indenyl fragment (Ru(2)−C(7) = 2.250(3) Å). Thus, compound **3**, isomeric with **2a**, is derived from two C−C bond-forming processes. Interestingly, the formerly free outer alkyne group of the starting material is now coordinated in π-fashion to the second Ru atom (Ru(1)−C(9) = 2.361(3) Å, Ru(1)−C(10) = 2.309(3) Å), effecting a small but significant elongation of the C−C triple bond (C(9)−C(10) = 1.2335 Å, cf. 1.172(6) Å in **1a**[3b]). Complexes containing η^1-indenyl ligands are relatively rare,[15] and in the present case the η^1-indenyl group may be stabilized by the presence of a 2-alkynyl substituent coordinated in π-fashion to the second ruthenium atom.

Compound **4** (Figure 3) is similarly formed from attack of the carbene at C_β and coupling of C_α and the *ortho* carbon of a Ph_2C phenyl ring. The latter leads to fusion of an indene ring system onto C_α and C_β of the C_4R ligand to give an η^1-indenyl unit, the structural data for which closely resemble that observed in **3**. In contrast to **3**, however, the $-C_\gamma{\equiv}C_\delta-$ functionality of the starting complex **1b** has now been incorporated into

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(6) Spectroscopic data for **2a**: IR (C_6H_{14}) ν(CO)/cm^{-1} 2081 s, 2059 vs, 2021 s, 2003 m, 1986 w; ^1H NMR ($CDCl_3$) δ 7.50−6.22 (m, 20H, Ph), 1.04 (s, 9H, Bu^t); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 122.8 (s). Anal. Calcd for $C_{39}H_{29}O_6PRu_2$: C, 56.66; H, 3.54. Found: C, 56.87; H, 3.62. Mp: 169 °C. Spectroscopic data for **2c**: IR (C_6H_{14}) ν(CO)/cm^{-1} 2083 s, 2061 vs, 2023 s, 2005 m, 1989 w; ^1H NMR ($CDCl_3$) δ 7.49−6.26 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 122.6 (s). Anal. Calcd for $C_{41}H_{25}O_6PRu_2$: C, 58.16; H, 2.98. Found: C, 58.07; H, 2.96. Mp: > 400 °C.

(7) Spectroscopic data for **3**: IR (C_6H_{14}) ν(CO)/cm^{-1} 2059 m, 2022 s, 1997 w, 1993 w, 1981 m; ^1H NMR ($CDCl_3$) δ 7.71−7.11 (m, 19H, Ph), 5.13 (d, J_{PH} = 6.8 Hz, 1H, CH), 1.28 (s, 9H, Bu^t); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 162.6 (s). Anal. Calcd for $C_{39}H_{29}O_6PRu_2$: C, 56.66; H, 3.54. Found: C, 56.87; H, 3.62. Mp: 155 °C.

(8) Spectroscopic data for **4**: IR (C_6H_{14}) ν(CO)/cm^{-1} 2090 s, 2072 vs, 2036 s, 2030 m, 2009 s, 1973 w; ^1H NMR ($CDCl_3$) δ 7.70−6.99 (m, 24H, Ph), 3.27 (d, J_{PH} = 4.7 Hz, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 88.8 (s). Anal. Calcd for $C_{41}H_{25}O_6PRu_2$: C, 58.16; H, 2.98. Found: C, 58.16; H, 2.91. Mp: 215 °C.

(9) Crystal data for **2a**: yellow prisms grown from diethyl ether/hexane at −20 °C; $C_{39}H_{29}O_6PRu_2{\cdot}C_4H_{10}O$, M_r = 900.9; monoclinic, space group $P2_1/n$, a = 12.073(2) Å, b = 9.735(2) Å, c = 34.805(5) Å, β = 93.05(1)°, V = 4084.6(13) Å^3, Z = 4, T = 200 K, D_c = 1.465 g cm^{-3}, $F(000)$ = 1824, λ = 0.710 73 Å, μ(Mo Kα) = 8.26 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.19 × 0.15 × 0.24 mm mounted on a Siemens R3m/V diffractometer by the ω-scan method ($2\theta < 48°$). An absorption correction (face-indexed numerical) was applied. Of 6431 reflections measured, 5266 were considered observed ($F > 6.0\sigma(F)$). The structure was solved (Patterson and Fourier methods) and refined (full-matrix least squares) using the Siemens SHELXTL PLUS program, giving final R and R_w values (based on $F_o{}^2$) of 0.0266 and 0.0302, respectively.

(10) Crystal data for **3**: hexagonal cylinders grown from hexane at −20 °C; $C_{39}H_{29}O_6PRu_2$, M_r = 826.8; monoclinic, space group $C2/c$, a = 31.8406(9) Å, b = 11.0622(4) Å, c = 20.2768(5) Å, β = 95.4480(23)°, V = 7109.8(5) Å^3, Z = 8, T = 295 K, D_c = 1.545 g cm^{-3}, $F(000)$ = 3322, λ = 1.540 56 Å, μ(Cu Kα) = 78.5 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.16 × 0.32 × 0.30 mm mounted on an Enraf-Nonius CAD4 diffractometer using the θ/2θ scan method ($3.0 < 2\theta < 140.0°$). An absorption correction (face-indexed numerical) was applied. Of 9242 reflections measured, 5891 were considered observed ($I > 2.5\sigma(I)$). The structure was solved (direct methods) and refined (full-matrix least squares) using the NRCVAX system, giving final R and R_w values of 0.032 and 0.044, respectively.

(11) Crystal data for **4**: red plates grown from hexane at −20 °C; $C_{41}H_{25}O_6PRu_2$, M_r = 846.7; triclinic, space group $P\bar{1}$, a = 11.108(1) Å, b = 11.267(1) Å, c = 15.642(1) Å, α = 91.696(7)°, β = 98.532(7)°, γ = 112.496(8)°, V = 1780.6(4) Å^3, Z = 2, T = 295 K, D_c = 1.579 g cm^{-3}, $F(000)$ = 844, λ = 0.710 73 Å, μ(Mo Kα) = 9.40 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.20 × 0.12 × 0.10 × 0.045 mm mounted on a Siemens R3m/V diffractometer by the ω-scan method ($2\theta < 50°$). Of 6619 reflections measured, 4892 were considered observed ($F > 6.0\sigma(F)$). The structure was solved and refined as for **2a** above, giving final R and R_w values of 0.0243 and 0.0262, respectively.

(12) See Chart 1 for designation of C_α, C_β, C_γ, and C_δ.

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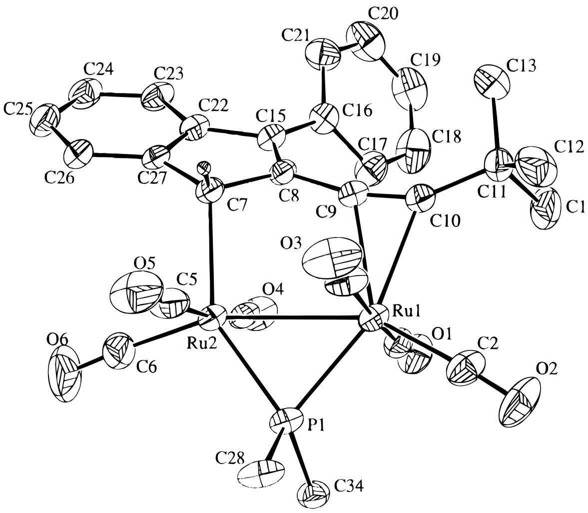

Figure 2. Molecular structure of $[Ru_2(CO)_6\{\mu\text{-}\eta^1,\eta^2\text{-}CH(C_6H_4)C(Ph){=}CC{\equiv}CBu^t\}(\mu\text{-}PPh_2)]$ (**3**) with the non-hydrogen atom labeling scheme. For clarity, only the *ipso* carbons of the *P*-phenyl rings are drawn. Important bond lengths (Å) and angles (deg) not mentioned in the text are as follows: Ru(1)−Ru(2) = 2.8928(4), C(7)−C(8) = 1.478(4), C(8)−C(9) = 1.428(4), C(10)−C(11) = 1.496(5), C(8)−C(15) = 1.387(4), C(15)−C(22) = 1.455(5), C(22)−C(27) = 1.399(5), C(27)−C(7) = 1.475(4); C(7)−C(8)−C(9) = 122.5(3), C(8)−C(9)−C(10) = 166.5(3), C(9)−C(10)−C(11) = 151.6(3), Ru(1)−P(1)−Ru(2) = 76.88(3), C(8)−C(15)−C(22) = 106.9(3), C(15)−C(22)−C(27) = 109.2(3), C(22)−C(27)−C(7) = 109.2(3)°.

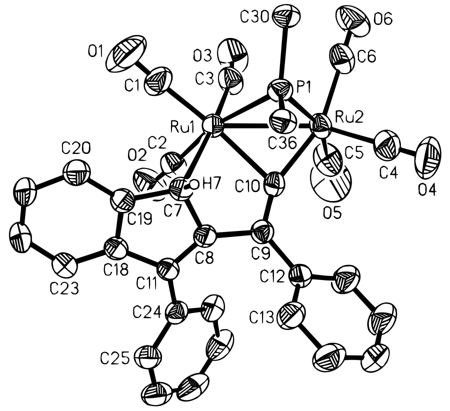

Figure 3. Molecular structure of $[Ru_2(CO)_6\{\mu\text{-}\eta^1,\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)(C_6H_4)CH\}(\mu\text{-}PPh_2)]$ (**4**) with the non-hydrogen atom labeling scheme. For clarity, only the *ipso* carbons of the *P*-phenyl rings are drawn. Important bond lengths (Å) and angles (deg) not mentioned in the text are as follows: Ru(1)−Ru(2) = 2.826(1), Ru(1)−C(7) = 2.291(3), C(7)−C(8) = 1.482(5), C(8)−C(9) = 1.481(5), C(8)−C(11) = 1.362(4), C(11)−C(18) = 1.464(5), C(18)−C(19) = 1.415(4), C(19)−C(7) = 1.482(5); Ru(1)−C(7)−C(8) = 99.9(2), C(7)−C(8)−C(9) = 114.6(2), C(8)−C(9)−C(10) = 110.7(3), C(9)−C(10)−Ru(1) = 118.3(3), Ru(1)−C(10)−Ru(2) = 84.7(1), Ru(1)−P(1)−Ru(2) = 73.4(1)°.

the organometallic structure with C(10) bridging the metal−metal bond, somewhat asymmetrically (Ru(1)−C(10) = 2.181(4) Å, Ru(2)−C(10) = 2.009(2) Å) to form a μ_2-vinylidene moiety (C(10)−C(9) = 1.326(4) Å). These bond parameters are in accord with those reported for $Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)$ (Ru(1)−C_α = 2.033(7) Å, Ru(2)−C_α = 2.026(7) Å, $C_\alpha{=}C_\beta$ = 1.326(11) Å) by Knox and co-workers.[16] The position of the butadiynyl-derived Ph substituent on C(9) occurs either as a result of $C_\beta-C_\gamma$ bond cleavage and subsequent coordination of C_γ to the Ru−Ru unit or by 1,2-phenyl migration with the original C_4 ligand remaining intact. Accounts of phenyl migration reactions are legion in organic chemistry,[17] and although there is precedent in the literature for metal-coordinated diyne cleavage,[18] such accounts are rare and the former seems a more likely course.

The generation of indenyl ring systems in **3** and **4** from **1a,b** via C−C bond formation at C_β and C_α resembles the recent synthesis of indenylidene from a CPh_2OSiMe_3-substituted diynyl ruthenium complex.[19] A plausible mechanism involves attack by the carbene Ph_2C: at C_β, creating a $C_\beta{=}C_{carbene}$ double bond and the highly electrophilic carbene center C_α. Subsequent electrophilic attack on the *ortho* carbon of a phenyl ring by C_α leads to C−C coupling and proton transfer to C_α.

The chemistry of **1a,b** toward amines[3b] and carbenes demonstrates an exclusive preference for nucleophilic attack at the coordinated and activated $C_\alpha-C_\beta$ alkyne bond over the unbound triple bond. Surprisingly, this is the first instance in which competitive reactivity of coordinated and free triple bonds in a diynyl complex has been put to the test. EHMO calculations on $Ru_2(CO)_6(\mu\text{-}\eta^1\text{:}\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}CC{\equiv}CH)(\mu\text{-}PH_2)$ suggest that in the ground state attack at C_α is favored on orbital control grounds, as found for **1a,b** with NEt_2H and $:CH_2$. Attack at C_α for the bulky carbene $:CPh_2$ is disfavored on steric grounds. In the transition state for the fluxional molecules, however, where the alkynyl fragment is perpendicular to the Ru−Ru vector, attack at C_β is favored on both orbital and charge grounds. We are examining the reactions of these interesting molecules with organic and metal-based electrophiles to further define their reactivity.

Acknowledgment. This work was supported by the National Research Council of Canada and by the Natural Sciences and Engineering Research Council (NSERC). P.B. gratefully acknowledges the NSERC for an International Fellowship Award. We thank Dr John F. Corrigan for his assistance with the EHMO calculations.

Supporting Information Available: Text giving full experimental details for the synthesis of compounds **2**−**4** and tables giving the structure determination summary, atomic coordinates, bond distances, bond angles, thermal parameters, and hydrogen atom positions for **2a**, **3**, and **4** (24 pages). Observed and calculated structure factor tables are available from the authors upon request. Ordering information is given on any current masthead page.

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