(Phthalimidomethyl)- and (Phenoxymethyl)cobalt Carbonyls. Equilibria of CO Insertion†

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*Summary: Phthalimidomethyl and phenoxymethyl as well as corresponding acetyl cobalt tetracarbonyls (**1**−**4**) were prepared and characterized. The single-crystal X-ray diffraction molecular structure of **1** (the first X-ray structure of an alkylcobalt tetracarbonyl with a pure organic alkyl group) was determined. The equilibrium constants of the equilibria **1** $\rightleftharpoons$ **2** and **3** $\rightleftharpoons$ **4** were determined at 20−60 and 20−40 °C, respectively.*

Cobalt carbonyls are the most traditional and even nowadays the most important type of carbonylation catalysts (e.g. for hydroformylation,[2] hydroxy- and alkoxycarbonylation,[2e,3] homologation,[4] cyclocarbonylation,[5] etc.). It is generally accepted that the mechanisms[6] of all of these reactions involve the formation of a cobalt−carbon bond in the reaction of the substrate (olefin, acetylene, functionalized alkyl or aryl derivatives) with the catalyst precursor cobalt compound, and an alkyl- or arylcobalt carbonyl is formed.

Surprisingly, in spite of the great practical importance of this reaction only a very limited amount of preparative work has been reported with alkylcobalt carbonyls. Structurally characterized derivatives have been mostly phosphine-substituted alkylcobalt carbonyls[7−13] and only one non-fluorinated alkyl complex: η^1-[η^6-(4-Me-$C_6H_4CH_2$)$Cr(CO)_3$]$Co(CO)_4$.[7]

Earlier studies of our groups showed that easy interconversion of sufficiently stable[14] alkyl- and acylcobalt complexes can be expected for derivatives of the XCH_2-$Co(CO)_3L$ and $XCH_2C(O)Co(CO)_3L$ type, where X is a polar organic group[7,11,12,15] or a heteroatom (Cl)[8]and L is CO or PPh_3. Although the decarbonylation of CH_3C-$(O)Co(CO)_4$ itself is disadvantageous under CO, its thermodynamic parameters could be determined.[16] These precedents led us to the study of the phthalimidomethyl and phenoxymethyl cobalt tetracarbonyls and their acetyl derivatives (**1**−**4**), which will be reported in this paper.

Experimental Section

The standard Schlenk inert-atmosphere technique was used. $Na[Co(CO)_4]$[17,18b] and phenoxyacetyl chloride were prepared according to published procedures.

IR spectra were obtained by a Carl Zeiss Jena IR 75 spectrophotometer and a Bruker FT-IR IFS 113V. ^1H and ^{13}C NMR spectra were registered on Varian Unity 300 MHz and Bruker AMX-400 (400 MHz) spectrometers.

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† Alkylcobalt Carbonyls. 12. Part 11: Reference 1.

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(1) Somlyai-Haász, J.; Haász, F.; Galamb, V.; Benedetti, A.; Zucchi, C.; Pályi, G.; Krümmling, T.; Happ, B.; Bartik, T. *J. Organomet. Chem.* **1991**, *419*, 205.

(2) (a) Pino, P.; Piacenti, F.; Bianchi, M. in *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 43. (b) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer: Heidelberg, Germany, 1980. (c) Markó, L. *Fundam. Res. Homogeneous Catal.* **1984**, *4*, 1. (d) Henrici-Olivé, G.; Olivé, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer: Berlin, 1984. (e) Cornils, B., Hermann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany, 1995.

(3) (a) Pino, P.; Piacenti, F.; Bianchi, M. in *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 233. (b) Alper, H. *Fundam. Res. Homogeneous Catal.* **1984**, *4*, 79. (c) Alper, H. *J. Organomet. Chem.* **1986**, *300*, 1.

(4) (a) Röper, M.; Loevenich, H. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Dordrecht, The Netherlands, 1983. (b) Tasi, M.; Pályi, G. *Magy. Kem. Lapja* **1986**, *41*, 190.

(5) Pályi, G.; Váradi, G.; Markó, L. in *Stereochemistry of Organometallic and Inorganic Compounds;* Bernal, I., Ed.; Elsevier: Amsterdam. 1986; Vol. 1, p 358.

(6) (a) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Kuhlman, L. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Flood, J. C. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 37. (d) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984**, *59*, 203. (e) des Abbayes, H. *New J. Chem.* **1987**, *11*, 535. (f) Alper, H. *Adv. Chem. Ser.* **1987**, *No. 326*, 8. (g) Solà, M.; Ziegler, T. *Organometallics* **1996**, *15*, 2611.

(7) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* **1986**, *108*, 3344.

(8) Galamb, V.; Pályi, G.; Boese, R.; Schmid, G. *Organometallics* **1987**, *6*, 861.

(9) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(10) Krümmling, T.; Bartik, T.; Markó, L.; Boese, R.; Schmid, G.; Vivarelli, P.; Pályi, G. *J. Organomet. Chem.* **1991**, *421*, 323.

(11) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(12) (a) Pályi, G.; Zucchi, C.; Bartik, T.; Herbrich, T.; Kriebel, C.; Boese, R.; Sorkau A.; Fráter, G. *Atti Accad. Sci. Bologna, Rend. Cl. Sci. Fis.* **1992/93**, *281* [14/10], 159. (b) Pályi, G.; Alberts, K.; Bartik, T.; Boese, R.; Fráter, G.; Herbrich, T.; Herfurth, A.; Kriebel, C.; Sorkau, A.; Tschoerner, C. M.; Zucchi, C. *Organometallics* **1996**, *15*, 3253.

(13) Ungváry, F.; Kovács, J.; Hammerschmitt, B.; Cordier, G. *Organometallics* **1993**, *12*, 2849.

(14) We mean here the kinetic stability against CO insertion−deinsertion, decomposition, or β-elimination in the sense of: Wilkinson, G. *Chimia* **1972**, *27*, 165.

(15) Sisak, A.; Sámpár-Szerencsés, E.; Galamb, V.; Németh, L.; Ungváry, F.; Pályi, G. *Organometallics* **1989**, *8*, 1096.

(16) Ungváry, F.; Markó, L. *Inorg. Chim. Acta* **1994**, *227*, 211.

(17) $Co_2(CO)_8$: Szabó, P.; Markó, L.; Bor, G. *Chem. Tech. (Leipzig)* **1961**, *13*, 549.

(18) (a) Hieber, W.; Vohler, O.; Braun, G. *Z. Naturforsch.* **1958**, *13b*, 192. (b) Galamb, V.; Pályi, G. In *Organometallic Syntheses* King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; Vol. 3, p 142.

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Table 1. Spectroscopic Data of Complexes 1–4

complex	IR ν(C—O) (hexane), cm^{-1}	^{1}H NMR, (benzene-d_6), δ	^{13}C NMR (benzene-d_6), δ
1	2107 (m), 2040 (s), 2029 (vs), 2020 (vs), 1723 (s)	4.24 (s, 2H, CH_2), 6.8 (m, 2H, β-CH); 7.4 (m, 2H, α-CH)	19.39 (CH_2), 123.57 (C_β), 133.44 (C_{ipso}), 134.38 (C_α), 167.41 (N—C=O), 197.87 (C≡O)
2	2112 (m),[a] 2053 (s), 2038 (vs), 2017 (vs), 1735 (s), 1715 (w, broad)	4.56 (s, 2H, CH_2), 6.8 (m, 2H, β-CH); 7.35 (m, 2H, α-CH)	60.47 (CH_2), 124.02 (C_β), 132.84 (C_{ipso}), 134.4 8 (C_α), 167.41 (N—C=O), 196.38 (C≡O), 221.99 (C=O)
3	2100 (m), 2042 (s), 2033 (vs, broad), 2019 (vs)	5.10 (s, CH_2), 6.7–7.3 (m, CH)	82.55 (CH_2), 115.88 (C_m), 123.02 (C_p), 130.66(C_o), 158.61 (C_{ipso}), 197.20 (C≡O)
4	2108 (m), 2055 (m, sh), 2011 (vs), 1710 (w)	4.14 (s, CH_2), 6.7–7.3 (m, CH)	62.25 (CH_2), 117.98 (C_m), 123.56 (C_p), 199.24 (C≡O), 226.72 (C=O)

[a] This band could be observed more clearly in a hexane–toluene mixture.

X-ray Structure Determination of 1: crystal dimensions 0.15 × 0.17 × 0.25 mm; Enraf-Nonius CAD4 diffractometer; graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) at 293(2) K; unit cell dimensions (from a least-squares fit of the setting angles of 25 randomly distributed reflections with $10° < \theta < 14°$ monoclinic, $P2_1/c$, a = 9.145(1) Å, b = 8.458(2) Å, c = 17.605(9) Å, β = 91.78(2)°, V = 1361.1(8) Å^3, Z = 4; $F(000)$ = 664; D_{calcd} = 1.616 g cm^{-3}; μ(Mo Kα) = 1.287 mm^{-1}; scan method ω scan; scan interval 1.0 + 0.35 tan θ; θ range 3–25°; data collected $-10 \le h \le 10$, $0 \le k \le 10$, $0 \le l \le 20$; no. of reflections collected 2368; no. of independent reflections 2368; crystal decay 16%; absorption correction ψ scan; no. of azimuthal reflections 3; maximum and minimum transmission 1.00 and 0.95; refinement method full-matrix least squares on F_o^2; observed reflection criterion all reflections; data/restraints/parameters 2366/0/214; R indices ($F_o > 4\sigma(F_o)$)[24] $R(F)$ = 0.0392, $R_w(F^2)$ = 0.0727; R indices (all data) $R(F)$ 0.0684, $R_w(F^2)$ = 0.0854; goodness of fit on F_o^2 1.033; largest difference peak and hole 0.267 and −0.170 Å^{-3}.

Molecular modeling calculations were performed with a 486 DX4-100 PC using the Hyperchem (Autodesk) program.

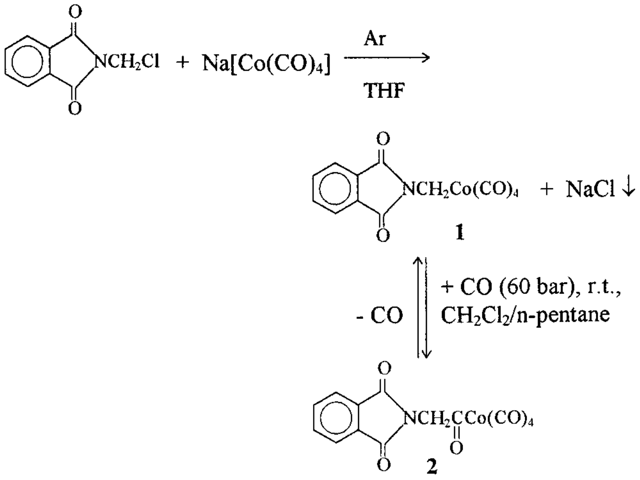
Preparation of the Complexes 1–4. To a solution of Na[Co(CO)$_4$] prepared from 0.86 g of $Co_2(CO)_8$ (2.5 mmol) and 30 g of 1.5% Na[Hg] in 9 mL of THF was added 0.978 g (5.0 mmol) of *N*-(chloromethyl)phthalimide at −78 °C under Ar. The reaction mixture was stirred for 1 h and then warmed to room temperature with continuous stirring (~1.5 h). The solvent was removed at 0 °C under reduced pressure, and *n*-pentane (30 mL) was added. Complex **1** was crystallized from this solution at first at −18 °C and then at −78 °C. Recrystallization from *n*-pentane gave 0.45 g (55%) of pale yellow crystals of **1**. Anal. Calcd for $C_{13}H_6CoNO_6$: C, 47.16; H, 1.83; Co, 17.80. Found: C, 47.5; H, 1.85; Co, 17.3.

A 0.05 M solution of **1** in *n*-hexane–dichloromethane (1:1) was pressurized to 60 bar of CO at room temperature in a stainless steel autoclave for 2 h and then chilled to −78 °C. IR analysis of the solution at −50 °C showed the quantitative transformation of **1** to a species having a spectrum typical for an acylcobalt tetracarbonyl (**2**). The crystallization of **2** was unsuccessful.

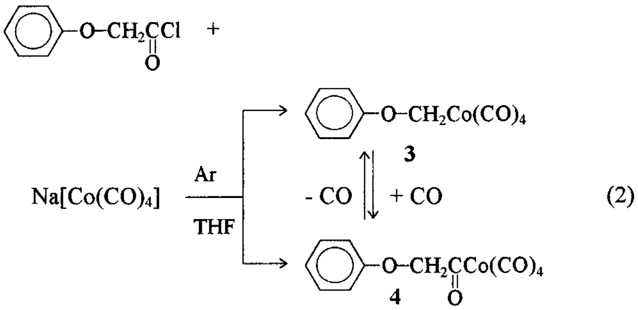
The preparation of complexes **3** and **4** was realized similarly. Compounds **3** and **4** were identified by IR and NMR spectra as well as through the isolation of the PPh$_3$ derivative of **4**, $PhOCH_2C(O)Co(CO)_3(PPh_3)$. Anal. Calcd for $C_{29}H_{22}O_5CoP$: C, 64.46; H, 4.10. Found: C, 64.5; H, 4.2. IR ν(C–O) in *n*-hexane: 2048 (m), 1984 (s), 1969 (s), 1712 (w) cm^{-1}. ^{1}H NMR in C_6D_6 (δ): 4.87 (s, 2H, CH_2) 6.8–6.9, 7.0–7.2, 7.5–7.6 (m, 20H, ar –CH) ppm. ^{13}C NMR in C_6D_6 (δ): 83.17 (CH_2, J_{C-P} = 29.08 Hz), 115.45 (C_m, Ph), 121.63 (C_p, Ph), 129.87 (C_o, Ph), 129.26 (C_m, PPh$_3$, J_{C-P} = 10.18), 131.19 (C_p, PPh$_3$, J_{C-P} = 2.31), 133.46 (C_o, PPh$_3$, J_{C-P} = 11.24), 133.58 (C_{ipso}, PPh$_3$, J_{C-P} = 42.99), 158.93 (C_{ipso}, Ph), 199.70 (CO_{carb}, J_{C-P} = 19.51), 234.46 (CO_{acyl}, J_{C-P} = 32.66) ppm. ^{31}P NMR in C_6D_6 (δ): 51.2 ppm.

Equilibrium Measurements. Approximately 0.05 M solutions were made from **1** (in toluene-d_8) and from the mixture of **3** and **4** (in benzene-d_6). Samples of the solutions (0.6 mL) were transferred by a gastight Hamilton syringe in a 5 mm 507-JY-7 NMR tube (Wilmad) under 750 mmHg pressure of CO. The tube was closed and held in a water bath at 20 °C with occasional shakings for 10 min before running the ^{1}H NMR experiment. The measurements were performed at 20, 30, 40, 50, and 60 °C for **1** and **2** and at 20, 30, and 40 °C for **3** and **4**. The equilibrium constants were calculated from the average ratios of alkyl- and acylcobalt tetracarbonyls measured during heating and cooling, respectively.

Scheme 1



Scheme 2



Results and Discussion

Compounds **1** and **4** were smoothly obtained by ion metathesis,[18] complex **2** was prepared by carbonylation of **1**, while the alkyl derivative **3** was obtained by decarbonylation of the corresponding acyl complex **4** (Schemes 1 and 2). Complex **1** could be isolated in analytically pure form; **2** was stable only in solution under CO pressure.[19] The reaction (2) shown in Scheme 2 yielded mixtures of complexes **3** and **4**, which could be enriched in **3** by decarbonylation and in **4** by

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(19) Preparation of compounds **1** and **2** was attempted at first by Beck and Petri;[20] only the PPh$_3$-substituted derivative of **2** has been isolated and characterized.

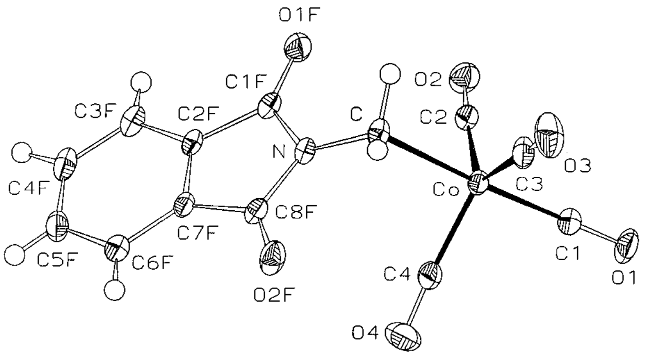

Figure 1. ORTEP view of **1** as determined by X-ray diffraction. Selected interatomic distances (pm) and angles (deg): Co−C(H$_2$), 207.5(3); C(H$_2$)−N, 144.1(4); Co−C(O)$_{eq}$, 181.3(5), 179.8(5), 179.6(4); Co−C(O)$_{ax}$, 181.8(4); Co−C(H$_2$)−N, 117.2(3); (O)C$_{ax}$−Co−C(H$_2$), 176.4(2); (O)C$_{eq}$−Co−C(H$_2$), 90.4(2), 83.4(2), 88.7(2).

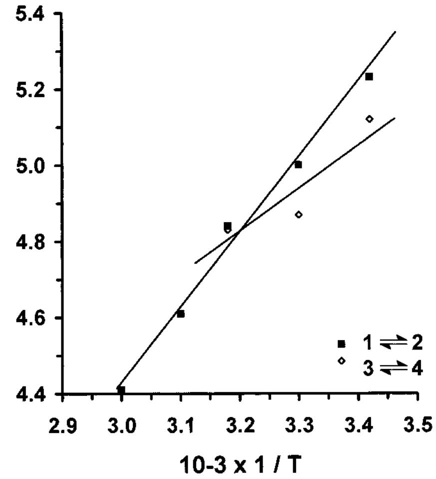

Figure 2. Temperature dependence of the equilibrium constants of the equilibria **1** ⇌ **2** (□) and **4** ⇌ **3** (◆).

carbonylation. All complexes were characterized by IR (ν(C−O)) ^{1}H NMR, and ^{13}C NMR spectroscopy (Table 1). Crystals suitable for X-ray diffraction analysis could be obtained from complex **1** (Figure 1).

Alkyl−acyl equilibria were studied by ^{1}H NMR. In the equilibrated mixture of **1** and **2** at 20 °C and under 1 bar of CO pressure in toluene-d_8 the ratio of the species was 1:1.5, while the ratio of **3** and **4** in benzene-d_6 was found to be very near 1:1. In comparison, the data reported for acetyl- and methylcobalt tetracarbonyl showed that under similar conditions the share of the methyl complex was only about 1%.[16] The qualitative or semiqualitative data published for phenyl-,[6d,7] methoxy-,[15] and ((trimethylsilyl)oxy)acetyl cobalt tetracarbonyls[15] and the corresponding alkyl complexes showed a behavior which is in accordance with the results of the present work.

Figure 2 shows the temperature dependence of the equilibrium constants of the decarbonylation of **2** and **4** as well. The thermodynamic parameters of both decarbonylations are listed in Table 2 together with literature data reported for the transformation of acetyl- into methylcobalt tetracarbonyl. The decarbonylations of **2** and **4** are much less endothermic than that of MeC(O)Co(CO)$_4$, which is in agreement with the qualitative preparative experience that the **1** ⇌ **2** and **4** ⇌ **3** equilibria can be much more easily shifted to one side or the other than in the case of the CH$_3$C(O)Co(CO)$_4$ ⇌ CH$_3$Co(CO)$_4$ equilibrium.[16,18a,21]

Table 2. Thermodynamic Parameters of the Decarbonylation of Acylcobalt Tetracarbonyls

complex	10^3K (20 °C)	$\Delta H°$, kJ/mol	$\Delta S°$, J/(mol K)	source
2	5.3	16.2 ± 0.9	7.9 ± 1.5	this work
4	6.7	11.8 ± 2.8	9.6 ± 4.0	this work
MeC(O)Co(CO)$_4$	0.06	46.9 ± 2.5	81.6 ± 8.4	ref 16

In spite of the crucial importance of alkylcobalt tetracarbonyls in mechanistic speculations,[6] the X-ray diffraction study on compound **1** is the first one concerning an alkylcobalt tetracarbonyl bound to a pure organic fragment. The ORTEP view of **1** shows that the cobalt has a trigonal-bipyramidal coordination geometry with an axial CH$_2$N alkyl group, as anticipated by spectroscopic analogies with related systems, staggered with respect to the equatorial (CO)$_3$ moiety.[6d,21b] The Co−C(alkyl) distance (207.5(3) pm) is intermediate between that in [η^1-(η^6-4-MeC$_6$H$_4$CH$_2$)Cr(CO)$_3$]Co(CO)$_4$ (212.6 pm)[22b] and in SF$_5$CH$_2$Co(CO)$_4$ (202.6(6) pm),[22c] the latter being close to the sum of the pertinent covalent radii (202 pm).[22,23]

The three equatorial carbonyl ligands are bent away from the axial one (average C$_{ax}$−Co−C$_{eq}$ = 92.6°), as commonly observed in such systems; however, only one of them is substantially bent toward the alkyl carbon atom (C−Co−C(3) = 83.4(2)°), since it can fit in the saddle of the CH$_2$ of the phthalimido group.

Molecular modeling calculations (Hyperchem, Autodesk), assuming tbp geometry around the Co, provided bond distance and bond angle values very close to those found experimentally by X-ray diffraction (cf. Supporting Information).

Supporting Information Available: Tables giving fractional atomic coordinates, anisotropic thermal parameters, bond distances and angles, and results of molecular mechanics calculations (4 pages). Ordering information is given on any current masthead page.

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(20) Beck, W.; Petri, W. *J. Organomet. Chem.* **1977**, *127*, C14.

(21) (a) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184. (b) Bor, G. *Inorg. Chim. Acta* **1967**, *1*, 81.

(22) (a) For [η^1-(η^3-cyclo-C$_5$F$_6$)Co(CO)$_3$]Co(CO)$_4$ (C−Co σ bond 197 pm), see: Hitchcock, P. B.; Mason, R. *Chem. Commun.* **1966**, 503. (b) For [η^1-(η^6-4-MeC$_6$H$_4$CH$_2$)Cr(CO)$_3$]Co(CO)$_4$, see ref 7. (c) For F$_5$SCH$_2$Co(CO)$_4$ (C−Co σ bond 202.6(6) pm), see: Damerius, R.; Leopold, D.; Schulze, W.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1989**, *578*, 110.

(23) (a) Capaccio, G.; Giacomello, P.; Giglio, E. *Acta Crystallogr., Sect. A* **1971**, *27*, 229. (b) Cser, F. *Acta Chim. Acad. Sci. Hung.* **1974**, *80*, 317. (c) Allinger, N.; Hirsch, J. A.; Miller, M. A.; Tyminsky, I. J. *J. Am. Chem. Soc.* **1969**, *91*, 337.

(24) $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, where $w = \sigma^2(F_o^2) + (0.0347P)^2 + 0.5240P$ and $P = (F_o^2 + {}^2F_c^2)/3$. GOF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.