the dissymmetric geometry of compounds **1** and **2** is much more easily recognizable, and for this reason we feel that the common structure for these two molecules should be regarded as pedagogically significant. Crystallization of each as the pure meso isomer results from continuous depletion from solution of the least soluble component in the equilibrium diastereomer distribution.

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Registry No. **1**, 80865-56-1; **2**, 7770-22-1.

Supplementary Material Available: Tables of best plane results, thermal parameters, and observed and calculated structure factor for **1** and **2** (22 pages). Ordering information is given on any current masthead page.

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Preparation, Structure, and Ligand Substitution Reactions of (Cycloocta-1,5-diene)(methyl *trans*-β-(phenylsulfonyl)acrylate)nickel

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The title compound was synthesized from bis(cycloocta-1,5-diene)nickel [Ni(cod)$_2$] and methyl *trans*-β-(phenylsulfonyl)acrylate (sma) in 88% yield and characterized by mass, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Its structure was determined by X-ray diffraction. The compound crystallizes from THF/Et$_2$O/pentane in the monoclinic space group C^5_{2h}—$P2_1/c$ with a = 8.428 (1) Å, b = 17.645 (4) Å, c = 12.168 (1) Å, β = 104.35 (1)°, and Z = 4. The structure was refined to R = 0.062 using 2616 unique data ($I < 2.0\sigma(I)$). The 16-electron complex is trigonal planar with the midpoints of the three coordinated C=C double bonds occupying vertices of a triangle centered at the nickel atom. Two of the double bonds are arranged perpendicular to the coordination plane, a conformation which has not yet been observed in d^{10} tris(olefin) complexes. Intramolecular distances indicate an anomalously short nonbonded contact between nickel and sulfur. Selective ligand substitution reactions can be achieved at room temperature or below. Treatment of the complex with diphosphines, 2,2′-bipyridine, 1,4-diazabuta-1,3-dienylbis(2,6-xylene), ethylenebis(dimethylamine), or an excess of 1,6-dimethylcycloocta-1,5-diene results in the liberation of the cod ligand, giving new NiL$_2$(sma) complexes. Maleic anhydride (mah) replaces the vinyl sulfone to give Ni(cod)(mah). When (cycloocta-1,5-diene)(dimethyl fumarate)nickel [Ni(cod)(fdm)] is treated with methyl *trans*-β-(phenylsulfonyl)acrylate (sma), the title compound is obtained in quantitative yield. Thus the coordinating ability of activated olefins increases in the order fdm < sma < mah.

Introduction

A wide variety of stoichiometric and catalytic reactions of unsaturated substrates are promoted or catalyzed by nickel(0) compounds.[1,2] A fascinating feature of these reactions is that they can be controlled by variation of the ligands attached to the nickel. For example, the so-called "naked nickel" (e.g., Ni(cod)$_2$ where cod = cycloocta-1,5-diene) catalyzes the cyclodimerization of methylenecyclopropane,[3] whereas the presence of phosphine-modified nickel(0) results in cyclotrimerization.[4] On the other hand, addition of special α,β-unsaturated carboxylic acid derivatives to nickel(0) leads to a remarkable enhancement of the cyclodimerization.[5] Unsaturated ligands such as these attract special attention since in some cases they act not only as controlling factors but also as cosubstrates.[6] It was therefore thought worthwhile to look for new ligands that might be able to play both parts.

It has recently been demonstrated that vinyl sulfones are useful synthons in organic chemistry. They can be used as ethylene,[7] acetylene,[8] or ketene[9] equivalents in Diels–Alder cycloadditions and 1,3-diyl trapping reactions.

We now have found that one chelating cod ligand in Ni(cod)$_2$ can be smoothly replaced by vinyl sulfones to give new thermally stable Ni(cod)(olefin) complexes whose behavior as catalysts is under investigation. In this paper we report the synthesis and structure of the title compound together with some related chemistry.

Experimental Section

General Remarks. All manipulations were carried out in oxygen-free, rigorously dried solvents under high-purity argon. The NMR spectrometers used were Bruker WP 80 FT (^{1}H and ^{31}P), Varian XL 100 FT (^{13}C), and Bruker WH 400 FT (^{1}H). ^{31}P positive chemical shifts are downfield from 85% H$_3$PO$_4$. IR spectra were run on a Nicolet FT IR 7199 spectrometer. The mass spectra were obtained on an Atlas-CH 5 spectrometer. Melting points were determined with a Büchi SMP-20 apparatus in ca-

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pillary tubes sealed under argon and are uncorrected. Microanalytical data for C, H, Ni, P, and S were provided by "Mikroanalytisches Laboratorium Dornis und Kolbe"; D-4330 Mülheim-Ruhr, West Germany.

Reagents. Published procedures were used to prepare Ni(cod)$_2$,[10] methyl *trans*-β-(phenylsulfonyl)acrylate (sma),[11] trimethylphosphine (PMe$_3$),[12] ethylenebis(dicyclohexylphosphine), (dcpe),[13] and 1,4-diaza-buta-1,3-dienylbis(2,6-xylene) (dad).[14] 1,6-Dimethylcycloocta-1,5-diene [dime-cod] was obtained by catalytic cyclodimerization of isoprene.[15] Cycloocta-1,5-diene (cod) (Chem. Werke Hüls, AG) and dimethyl fumarate (fdm) (Merck-Schuchardt) were distilled and stored under argon. Maleic anhydride (mah) (Merck-Schuchardt) was vacuum distilled, recrystallized from rigorously dried Et$_2$O, and stored under argon. Ethylenebis(dimethylamine) (tmeda) (Merck-Schuchardt) was distilled over KOH and stored under argon. 2,2′-Bipyridine (bpy) (Merck AG) and ethylenebis(dimethylphosphine) (dmpe) (Strem Chemicals, Inc.) were stored under argon without further purification. Celite 545 (Fluka AG, Buchs) was stored at ca. 100 °C.

Preparation of (Cycloocta-1,5-diene)(methyl *trans*-β-(phenylsulfonyl)acrylate)nickel (1). To a mixture of Ni(cod)$_2$ (7.37 g, 26.8 mmol) and sma (6.78 g, 30 mmol) was added THF (20 mL). A deep red solution was obtained, which was stirred for 4 h at 22 °C. The solution was cooled to −35 °C for ca. 12 h. A solid was obtained, which was separated by filtration, washed with Et$_2$O (3 × 20 mL), and dried under vacuum (10^{-3} torr) to yield orange-red crystals of **1**: 9.18 g (88%); mp 147 °C: mass spectrum (70 eV), *m/z* (for ^{58}Ni) 392 (M$^+$, relative intensity 1%), 226 (4), 125 (100), 80 (18), 77 (42), 54 (51); IR (KBr) ν 1684 (C=O), 1549, 1536 (C=C), 1221 (COC), 1299, 1126 cm^{-1} (SO$_2$); ^{1}H NMR (400 MHz, toluene-d_8, −30 °C) δ 7.89 (m, 2 H), 6.87 (m, 3 H), 6.25 (m, 1 H, ^3J = 8 Hz), 5.47 (m, 1 H), 5.08 (m, 1 H, ^3J = 8 Hz), 4.72 (m, 1 H), 4.07 (d, 1 H, ^3J = 10.9 Hz), 3.55 (d, 1 H), 3.23 (s, 3 H), 2.16 (m, 1 H), 2.01 (m, 1 H), 1.79 (m, 2 H), 1.60 (m, 4 H); ^{13}C NMR (25.2 MHz, THF-d_8) δ 171.0 (s), 145.3 (s), 132.4 (d, ^1J(CH) = 162 Hz), 129.6 (d, 162), 127.2 (d, 165), 106.9 (d, 159), 105.1 (d, 157), 104.4 (d, 156), 63.0 (d, 167), 51.0 (q, 145), 45.1 (d, 162), 30.2 (t, 130). Anal. Calcd for $C_{18}H_{22}NiO_4S$: C, 54.99; H, 5.64; Ni, 14.93; M_r, 393.15. Found: C, 55.13; H, 5.63; Ni, 14.93.

Reactions of (Cycloocta-1,5-diene)(methyl *trans*-β-(phenylsulfonyl)acrylate)nickel (1). General Procedure. To a stirred red solution of Ni(cod)(sma) in THF was added dropwise (between 0 and 22 °C) a solution of the corresponding ligand in THF. After the solution was stirred for ca. 1 h, volatiles were removed by distillation (10^{-3} torr). The remaining residue was recrystallized from appropriate solvents. The crystals so obtained were isolated by filtration or by use of a flame-drawn glass syphon, washed with cold Et$_2$O, and dried under vacuum.

With dime-cod: 0.77 g (1.96 mmol) of **1** and 3.5 mL of dime-cod gave, after recrystallization from Et$_2$O at −35 °C, 0.48 g of red needles of **2** (58%): mass spectrum (70 eV), *m/z* (for ^{58}Ni) 420 (M$^+$, relative intensity 1%), 226 (1), 194 (5), 162 (1), 136 (13), 125 (44), 68 (100); IR (KBr) ν 1690 (C=O), 1220 (COC), 1300, 1130 cm^{-1} (SO$_2$); ^{1}H NMR (ca. 11% of a second isomer has been detected) (400 MHz, toluene-d_8, 25 °C) δ 7.85 (m, 2 H), 6.90 (m, 3 H), 6.02 (m, 1 H), 5.10 (m, 1 H), 3.59 (d, 1 H, ^3J = 10.6 Hz), 3.32 (d, 1 H), 3.19 (s, 3 H), 2.56–1.60 (br, 8 H), 2.08 (s, 3 H), 1.50 (s, 3 H). Anal. Calcd for $C_{20}H_{26}NiO_4S$: C, 57.03; H, 6.22; Ni, 13.94; S, 7.61; M_r, 421.20. Found: C, 57.11; H, 6.20; Ni, 14.04; S, 7.58.

With dmpe: 1.28 g (3.26 mmol) of **1** and 0.49 g (3.26 mmol) of dmpe gave, after recrystallization from Et$_2$O/THF (1/1) at −35 °C, 0.82 g of yellow-orange needles of **3**: 59%, mp 48 °C; mass spectrum (70 eV), *m/z* (for ^{58}Ni) 434 (M$^+$, relative intensity 7%), 293 (31), 208 (100), 180 (63), 134 (27), 77 (16); IR (KBr) ν 1680 (C=O), 1215 (COC), 1288, 1126 cm^{-1} (SO$_2$); ^{31}P NMR (32 MHz, toluene-d_8, −60 °C) δ 28.1, 25.1 (J_{PP} = 37.2 Hz); ^{1}H NMR (80 MHz, toluene-d_8) δ 8.1 (m, 2 H), 7.10 (m, 3 H), 4.27 (m, 1 H, ^3J = 10.5 Hz), 3.69 (m, 1 H), 3.33 (s, 3 H), 1.23–0.70 (br, 16 H). Anal. Calcd for $C_{16}H_{26}NiO_4P_2S$: C, 44.17; H, 6.02; Ni, 13.49; M_r, 435.11. Found: C, 44.51; H, 6.00; Ni, 13.43.

With dcpe: 0.61 g (1.55 mmol) of **1** and 0.65 g (1.55 mmol) of dcpe gave, after crystallization with Et$_2$O, 0.82 g of yellow crystals of **4**: 75%; mp 220 °C; mass spectrum (70 eV), *m/z* (for ^{58}Ni) 706 (M$^+$, relative intensity 11%), 480 (100), 398 (32), 316 (23), 234 (24), 152 (23), 55 (37); IR (KBr) ν 1690 (C=O), 1210 (COC), 1290, 1130 cm^{-1} (SO$_2$); ^{31}P NMR (32 MHz, THF–d_8) δ 69.7, 67.0 (J_{PP} = 29.8 Hz); ^{1}H NMR (80 MHz, THF-d_8) δ 7.90 (m, 2 H), 7.45 (m, 3 H), 3.72 (m, 1 H, ^3J = 10.0, J_P = 5.5 and 2.5 Hz), 3.40 (s, 3 H), 3.12 (m, 1 H, J_P = 1.5 and 7.0 Hz), 2.0–1.0 (br, 48 H). Anal. Calcd for $C_{36}H_{58}NiO_4P_2S$: C, 61.11; H, 8.26; Ni, 8.30; M_r, 707.58. Found: C, 61.20; H, 8.24; Ni, 8.28.

With PMe$_3$. In a NMR tube **1** and PMe$_3$ (1/1 ratio) were dissolved in C$_6$D$_6$ at 22 °C. The ^{1}H NMR spectrum (80 MHz) obtained was that of a 1/1 mixture of **1** and Ni(PMe$_3$)$_2$(sma). Ni(PMe$_3$)$_2$(sma): δ 8.05 (m, 2 H), 6.94 (m, 3 H), 4.06 (m, 1 H), 3.21 (s, 3 H), 3.20 (m, 1 H), 1.20 (d, 9 H, J_P = 7 Hz), 0.93 (d, 9 H, J_P = 7 Hz).

With bpy: 0.82 g (2.09 mmol) of **1** and 0.33 g (2.09 mmol) of bpy gave 0.90 g of copper-red crystals of **5**: 90%; mp 147 °C; mass spectrum (70 eV), the compound vaporized under decomposition, products of thermolysis were *m/z* 226 (sma) and *m/z* 156 (bpy); IR (KBr) ν 1680 (C=O), 1205 (COC), 1274, 1130 cm^{-1} (SO$_2$); ^{1}H NMR (400 MHz, dimethylformamide-d_7) δ 9.51 (m, 1 H), 8.78 (m, 1 H), 8.46 (m, 2 H), 8.24 (m, 2 H), 7.92 (m, 2 H), 7.72 (m, 2 H), 7.62 (m, 1 H), 7.59 (m, 2 H), 3.62 (m, 2 H, THF), 3.48 (s, 3 H), 3.35 (d, 1 H, ^3J = 9.6 Hz), 2.85 (d, 1 H), 1.77 (m, 2 H, THF). Anal. Calcd for $C_{20}H_{18}N_2NiO_4S\cdot(C_4H_8O)_{0.5}$: C, 55.37; H, 4.65; N, 5.87; Ni, 12.30; S, 6.72; M_r, 477.21. Found: C, 55.40; H, 4.67; N, 5.38; Ni, 12.99; S, 6.20.

With dad: 0.62 g (1.58 mmol) of **1** and 0.42 g (1.58 mmol) of dad gave, after recrystallization from THF at −35 °C, 0.82 g of dark blue crystals of **6**: 95%, mp 194 °C; mass spectrum (70 eV), *m/z* (for ^{58}Ni) 548 (M$^+$, relative intensity 1.5%), 322 (38), 249 (100), 132 (63), 125 (71), 77 (44); IR (KBr) ν 1670 (C=O), 1225 (COC), 1300, 1130 cm^{-1} (SO$_2$); ^{1}H NMR (80 MHz, THF-d_8) δ 9.16 (s, 1 H), 9.05 (s, 1 H), 7.59 (m, 2 H), 7.30 (m, 9 H), 3.16 (d, 1 H, ^3J = 10.5 Hz), 3.08 (s, 3 H), 2.74 (d, 1 H), 2.51 (s, 3 H), 2.41 (s, 6 H), 2.14 (s, 3 H). Anal. Calcd for $C_{28}H_{30}N_2NiO_4S$: C, 61.22; H, 5.50; N, 5.10; Ni, 10.69; S, 5.84; M_r, 549.34. Found: C, 61.04; H, 5.48; N, 5.03; Ni, 10.73; S, 5.93.

With tmeda: 0.80 g (2.03 mmol) of **1** and 0.236 g (∼0.30 mL, 2.03 mmol) of tmeda gave, after recrystallization from Et$_2$O/toluene/THF (30/30/20 mL) at −78 °C, 0.52 g of dark red crystals of **7**: 64%; mp 179 °C; mass spectrum (70 eV), *m/z* (for ^{58}Ni) 400 (M$^+$, relative intensity 1%), 174 (4), 125 (52), 77 (19), 58 (100); IR (KBr) ν 1660 (C=O), 1230 (COC), 1270, 1130 cm^{-1} (SO$_2$); ^{1}H NMR (80 MHz, THF-d_8) δ 7.79 (m, 2 H), 7.40 (m, 3 H), 3.34 (s, 3 H), 2.90 (s, 3 H), 2.83 (s, 3 H), 2.71 (s, 3 H), 2.59 (d, 1 H, ^3J = 9 Hz), 2.48 (s, 3 H), ca. 2.70–2.10 (br, 4 H), 2.05 (d, 1 H). Anal. Calcd for $C_{16}H_{26}N_2NiO_4S$: C, 47.90; H, 6.53; N, 6.98; Ni, 14.63; M_r, 401.17. Found: C, 48.00; H, 6.51; N, 6.98; Ni, 14.49.

With mah: 0.36 g (0.92 mmol) of **1** and 0.09 g (0.92 mmol) of mah at −20 °C gave, after recrystallization from THF/Et$_2$O (1/1, ca. 10 mL) at −78 °C, 0.21 g of red-brown crystals of **8**: 86%, mp 145–150 °C dec; mass spectrum (70 eV), the compound vaporized under decomposition, products of thermolysis were *m/z* 108 (cod) and *m/z* 98 (mah); IR (KBr) ν 1790, 1780 (sh), 1750 (sh), 1720 (sh), 1710 cm^{-1} (C=O); ^{1}H NMR (80 MHz, THF-d_8) δ 5.20 (s(br), 4 H), 3.43 (s, 2 H), 2.38 (s(br), 8 H). Anal. Calcd for $C_{12}H_{14}NiO_3$: C, 54.40; H, 5.33; Ni, 22.16; M_r, 264.95. Found: C, 54.10; H, 5.30; Ni, 22.22.

Preparation of (Cycloocta-1,5-diene)(dimethyl fumarate)nickel [Ni(cod)(fdm)] and Its Reaction with Methyl *trans*-β-(Phenylsulfonyl)acrylate (sma). A solution of dimethyl fumarate (0.60 g, 4.14 mmol) in THF (30 mL) was added dropwise to a stirred yellow solution/suspension of Ni(cod)$_2$ (1.14 g, 4.14 mmol) in THF (60 mL) at 0 °C. The orange-red solution so obtained was stirred at 22 °C for 20 min. Volatiles were pumped off to leave an orange-red powder, which was dissolved in Et$_2$O (30 mL), filtered through a 3-cm Celite pad, and cooled overnight at −35 °C. Red crystals were isolated as described above: yield 0.90 g (70%); mp 106–108 °C; mass spectrum (70 eV), *m/z*

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Table II. Final Atomic Coordinates and Their Standard Deviations (×10^4)

atom	*x*	*y*	*z*
Ni	3970 (1)	919 (1)	2326 (1)
S	5201 (1)	2222 (1)	1131 (1)
O(1)	7691 (4)	175 (2)	3159 (3)
O(2)	6699 (4)	−510 (2)	1577 (3)
O(3)	5083 (4)	2892 (2)	1807 (3)
O(4)	3792 (4)	1986 (2)	271 (3)
C(1)	5835 (5)	1471 (3)	2039 (4)
C(2)	5748 (5)	721 (3)	1589 (4)
C(3)	6830 (5)	123 (3)	2216 (4)
C(4)	7680 (7)	−1139 (3)	2124 (5)
C(5)	6811 (5)	2384 (3)	448 (4)
C(6)	7878 (7)	2972 (3)	799 (5)
C(7)	9205 (7)	3058 (4)	323 (6)
C(8)	9433 (7)	2576 (4)	−497 (5)
C(9)	8331 (7)	1994 (4)	−869 (5)
C(10)	6997 (6)	1902 (3)	−407 (4)
C(11)	2072 (6)	1623 (3)	2611 (4)
C(12)	3138 (6)	1467 (3)	3602 (5)
C(13)	3034 (8)	852 (4)	4408 (5)
C(14)	2352 (7)	92 (3)	3891 (5)
C(15)	2941 (6)	−79 (3)	2847 (5)
C(16)	2165 (6)	100 (3)	1761 (5)
C(17)	634 (6)	558 (3)	1368 (5)
C(18)	476 (6)	1215 (3)	2146 (5)

(for ^{58}Ni) 310 (M$^+$, relative intensity 4%), 113 (100), 85 (44), 54 (70); IR (KBr) ν 1720, 1690 cm^{-1} (C=O); ^{1}H NMR (80 MHz, toluene-d_8, −30 °C) δ 4.81 (m, 4 H), 3.70 (s, 2 H), 3.37 (s, 6 H), 1.61 (m, 8 H). Anal. Calcd for $C_{14}H_{20}NiO_4$: C, 54.07; H, 6.48; Ni, 18.88; M_r 311.02. Found: C, 54.23; H, 6.50; Ni, 19.10.

To a stirred solution of Ni(cod)(fdm) (0.60 g, 1.93 mmol) in Et_2O (30 mL) at 0 °C was added dropwise a solution of sma (0.436 g, 1.93 mmol) in Et_2O (40 mL). The solution was stirred for 2 h whereby orange microcrystals precipitated. These were isolated by filtration, washed with pentane (2 × 10 mL), and dried under vacuum; yield 0.73 g (96%). IR and ^{1}H NMR spectra were identical with those of compound 1.

Structure Determination of Ni(cod)(sma) (1). Collection and Reduction of X-ray Data. Dark red crystals were obtained upon recrystallization from THF/Et_2O/pentane at −35 °C. A suitable crystal was sealed under argon in a glass capillary. Diffraction experiments were performed with a Nonius CAD 4/PDP 8 four-circle automated diffractometer using Cu Kα radiation. Data collection parameters are summarized in Table I. The final orientation matrix and unit cell parameters were determined from 75 machine-centered reflections. Three standard reflections (0,−5,−3; 0,−5,5; 3,−2,2), examined after every 90 measurements, showed no signs of decay during the course of collection. Data reduction was carried out as described previously.[16] No absorption correction was applied. The systematic absences *h*0*l* ($l \neq 2n$) and 0*k*0 ($k \neq 2n$) are consistent with the monoclinic space group $P2_1/c$.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom technique and refined initially with the program SHELX.[17] A difference density synthesis confirmed the structure and yielded reasonable positions for all H atoms. The structure was then refined by full-matrix least squares[16] allowing all atoms except H anisotropic thermal motion (217 parameters refined). Refinement converged at R (R_w) = 0.062 (0.074). The final difference Fourier synthesis was essentially flat with the largest peaks ($\Delta F \leq 0.92$ e Å^{-3}) in the vicinity of the nickel atom. Positional parameters of the non-hydrogen atoms and interatomic distances and angles are presented in Tables II and V, respectively. See paragraph at the end of this article regarding available supplementary material.

Table III. Decomposition Temperatures of Selected Nickel Olefin Complexes

complex	dec temp, °C	ref
$Ni(CH_2{=}CHC_6H_5)_3$	ca. −20	19
$Ni(CH_2{=}CHCO_2Me)_2$	ca. −10	20
$Ni(CH_2{=}CH_2)_3$	ca. 0	21
Ni(cod)($CH_2{=}CHCO_2Me$)	*a*	20
Ni(cod)(*trans*-$EtO_2CCH{=}CHCO_2Et$)	ca. 85–90	22
$Ni(CH_2{=}CHCN)_2$	ca. 100	23
Ni(cod)(*trans*-$MeO_2CCH{=}CHSO_2Ph$)	ca. 180	this work

[a] Stable below room temperature.

Table IV. ^{13}C NMR Data[a]

compd	δ(C=C)	$\Delta\delta$(C=C)	^1J(C–H), ±2 Hz
cod[37]	128.7		
$Ni(cod)_2$[37]	89.7	−39.0	
Ni($\underline{\text{cod}}$)(sma)	104.4	−24.3	156
	105.1	−23.6	157
	106.9	−21.8	159
Ni(cod)($\underline{\text{sma}}$)	63.0	−80.3	167
	45.1	−85.3	162
sma	143.3		182
	130.4		172

[a] 25.2 MHz; room temperature.

Results and Discussion

Preparation and Physical Characteristics of Ni(cod)(sma).

The following reaction (eq 1) gave the title compound in 88% yield, where cod = cycloocta-1,5-diene

$$Ni(cod)_2 + sma \xrightarrow[-cod]{THF,\ 22\ °C} Ni(cod)(sma) \qquad (1)$$

and sma = methyl *trans*-β-(phenylsulfonyl)acrylate ($MeO_2CCH{=}CHSO_2Ph$). Even with an excess of sma, the second cod ligand could not be replaced. However, when Ni(cdt) was used as starting material (where cdt = *trans,trans,trans*-cyclododeca-1,5,9-triene), $Ni(sma)_2$ could be isolated in 13% yield.[18] The dark red crystals of Ni(cod)(sma) are soluble in THF and aromatic hydrocarbons. They are sparingly soluble in Et_2O and nearly insoluble in saturated hydrocarbons. Ni(cod)(sma) proves to be surprisingly thermally stable compared with known nickel olefin complexes (cf. Table III). It has a sharp melting point at 147 °C and starts to decompose at ca. 180 °C. Its high stability probably stems from a favorable combination of electron-donating and electron-withdrawing olefinic ligands attached to the nickel atom.[19] The ^{1}H NMR spectrum exhibits a wide range of resonances for the olefinic cod protons. Two signals are shifted to high field (δ 5.08 and 4.72), and the other two protons resonate at δ 5.47 (which is the value of uncomplexed cod) and δ 6.25, respectively. This observation can be interpreted[24] as an anisotropic effect caused by the SO_2 group for the following reasons: The ^{1}H NMR spectrum shows no solvent dependence, and no bands in the region of uncomplexed C=C double bonds are present in the IR spectra (KBr disk or THF solution); the values of the carbonyl stretching frequency (1684 cm^{-1}; uncomplexed sma 1720 cm^{-1}) and the symmetric and asymmetric sulfonyl stretching fre-

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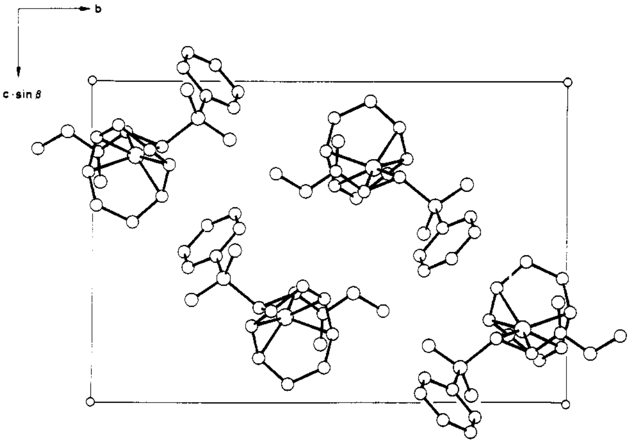

Figure 1. Projection of the unit cell along −*a*.

quencies (1299 and 1126 cm^{-1}; uncomplexed sma 1300 and 1150 cm^{-1}) strongly suggest that there is no bonding interaction between these two functional groups and the nickel atom. This explanation is in accordance with the results of the X-ray analysis (vide infra). At ca. 60 °C, the four cod protons give rise to one broad signal, which can be attributed to rotation of the sma ligand. The barrier for rotation lies in the range expected for a d^{10} L_2M(olefin) complex (76–105 kJ mol^{-1}).[25]

The results of the ^{13}C NMR analysis are brought together in Table IV. The $\Delta\delta$ values for sma are normal for electron-deficient olefins attached to nickel(0);[26] the $\Delta\delta$ values of cyclooctadiene in Ni(cod)(sma) are rather low, indicating very weak back-bonding. ^1J(C–H) of sma is reduced on coordination to 162 and 167 Hz. Ester methyl ^1J(C–H) of 145 Hz is typical for esters and is unaffected by coordination.

Description and Discussion of the Structure of Ni(cod)(sma) (1). The crystal structure consists of the packing of discrete molecules as can be seen from Figure 1. The molecular structure is shown in Figure 2 together with the arbitrary numbering scheme. A projection of the structure along the vector from the midpoint of the sma C=C double bond to the nickel atom is also shown. Selected bond lengths, bond angles, and torsional angles are given in Table V. The cod unit is linked to the nickel atom through two π bonds with an average Ni–C distance of 2.115 (7) Å. In the cod ligand the average C=C double bond length is 1.351 (8) Å and the average C–C single bond length is 1.508 (8) Å. These data indicate that the cod ligand in Ni(cod)(sma) is not as strongly bound as in $Ni(cod)_2$.[27] This is in accordance with the observed ^{13}C NMR data. There is no significant difference in length between the two double bonds, and their bonding modes with nickel are similar. The midpoints M(1) and M(2) of the two double bonds lie in the nickel coordination plane together with C(1) and C(2) of sma (maximum deviation 0.034 Å). The Ni–C(1) and Ni–C(2) distances are 1.953 (4) and 1.966 (5) Å, respectively. These values are comparable to those found in $Ni(PPh_3)_2(PhCOCH{=}CHCO_2Me)$ and related compounds.[28] The asymmetry of Ni–C bond lengths, sometimes observed in such complexes,[29] cannot be discussed considering their errors. Coordination of sma to the nickel atom has the expected effect of lengthening of C=C double bond C(1)–C(2) to 1.430 (7) Å, which is comparable with known data.[28] Sma also distorts considerably from planarity, the major distortion being the bending back of the carboxymethyl and sulfonyl groups from the nickel atom. A quantitative measurement of this distortion for trans disubstituted olefins commonly involves the torsional angles about the C=C bond.[30] Figure 3 illustrates the angles δ, δ′, and γ, where δ and δ′ are the torsional angles NiC=CR for each substituent and γ is the RC=CR torsional angle. As bending back occurs, δ and δ′ increase from 90° while γ decreases from 180°. The present values are δ = 103.4°, δ′ = 100.3°, and γ = 156.3°.

The twist of sma out of the coordination plane is illustrated by the angle between normals to the planes Ni-C(1)-C(2) and Ni-M(1)-M(2). The corresponding value is

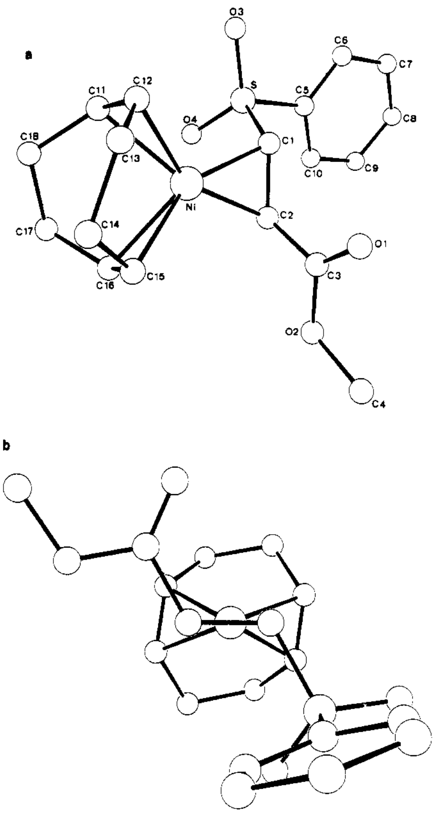

Figure 2. Molecular structure of Ni(cod)(sma). (a) General view showing the arbitrary numbering scheme. (b) View along the vector joining the midpoint of the olefinic C=C bond of the sma ligand and the nickel atom.

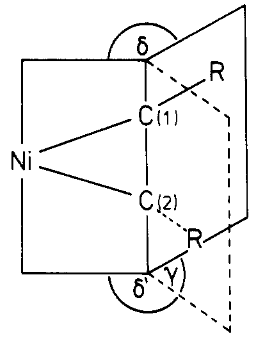

Figure 3. Illustration of the angles δ, δ′, and γ.

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Table V. Distances (Å) and Angles (deg) in Ni(cod)(sma)

Bond Distances

Ni-C(1)	1.953 (4)	O(2)-C(3)	1.351 (6)	C(11)-C(12)	1.342 (8)
Ni-C(2)	1.966 (5)	O(2)-C(4)	1.444 (7)	C(11)-C(18)	1.507 (7)
Ni-C(11)	2.121 (5)	C(1)-C(2)	1.430 (7)	C(12)-C(13)	1.480 (9)
Ni-C(12)	2.092 (6)	C(2)-C(3)	1.482 (7)	C(13)-C(14)	1.534 (9)
Ni-C(15)	2.128 (5)	Ni· · ·S	3.074 (4)	C(14)-C(15)	1.505 (8)
Ni-C(16)	2.087 (5)	C(5)-C(6)	1.370 (7)	C(15)-C(16)	1.359 (8)
S-O(3)	1.457 (4)	C(5)-C(10)	1.384 (7)	C(16)-C(17)	1.498 (7)
S-O(4)	1.437 (4)	C(6)-C(7)	1.390 (9)	C(17)-C(18)	1.523 (8)
S-C(1)	1.725 (5)	C(7)-C(8)	1.360 (9)	Ni· · ·O(1)	3.318 (4)
S-C(5)	1.782 (5)	C(8)-C(9)	1.384 (9)	Ni· · ·O(4)	3.104 (4)
O(1)-C(3)	1.200 (6)	C(9)-C(10)	1.386 (8)		

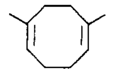
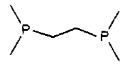
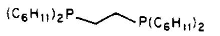
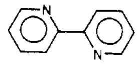
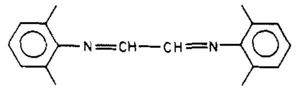
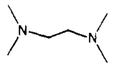
Bond Angles

C(1)-Ni-C(2)	42.8 (2)	Ni-C(2)-C(3)	109.1 (3)	Ni-C(11)-C(18)	107.3 (3)
C(11)-Ni-C(12)	37.1 (2)	H(2)-C(2)-C(1)	119.4 (5)	C(12)-C(11)-C(18)	125.2 (5)
C(15)-Ni-C(16)	37.6 (2)	H(2)-C(2)-C(3)	118.7 (4)	Ni-C(12)-C(11)	72.6 (3)
O(3)-S-O(4)	119.1 (2)	C(2)-C(3)-O(1)	126.3 (5)	Ni-C(12)-C(13)	103.8 (4)
O(3)-S-C(5)	107.5 (2)	C(2)-C(3)-O(2)	109.7 (4)	C(11)-C(12)-C(13)	127.6 (5)
O(4)-S-C(5)	107.1 (2)	O(1)-C(3)-O(2)	123.9 (4)	C(12)-C(13)-C(14)	116.5 (5)
C(1)-S-O(3)	108.4 (1)	S-C(5)-C(6)	119.6 (4)	C(13)-C(14)-C(15)	110.7 (5)
C(1)-S-O(4)	108.3 (2)	S-C(5)-C(10)	119.6 (4)	Ni-C(15)-C(14)	109.2 (4)
C(1)-S-C(5)	105.7 (2)	C(6)-C(5)-C(10)	120.8 (5)	Ni-C(15)-C(16)	69.6 (3)
C(3)-O(2)-C(4)	114.5 (4)	C(5)-C(6)-C(7)	119.1 (5)	C(14)-C(15)-C(16)	126.5 (5)
Ni-C(1)-C(2)	69.1 (3)	C(6)-C(7)-C(8)	120.8 (6)	Ni-C(16)-C(15)	72.8 (3)
Ni-C(1)-S	111.3 (2)	C(7)-C(8)-C(9)	119.9 (6)	Ni-C(16)-C(17)	103.4 (4)
H(1)-C(1)-S	114.6 (4)	C(8)-C(9)-C(10)	120.1 (5)	C(15)-C(16)-C(17)	127.3 (5)
H(1)-C(1)-C(2)	115.8 (4)	C(9)-C(10)-C(5)	119.1 (5)	C(16)-C(17)-C(18)	114.4 (5)
Ni-C(2)-C(1)	68.1 (3)	Ni-C(11)-C(12)	70.2 (3)	C(17)-C(18)-C(11)	113.0 (4)

Torsional Angles

Ni-C(2)-C(1)-S	103.4	S-C(1)-C(2)-C(3)	156.3	H(1)-C(1)-C(2)-H(2)	-148.1
Ni-C(1)-C(2)-C(3)	100.3	S-C(1)-C(2)-H(2)	-5.3	C(1)-C(2)-C(3)-O(1)	8.2

Table VI. Summary of Ligand Substitution Reactions of Ni(cod)(sma)

compd	L_2	color	mp, °C	yield, %
2	 (dime-cod)	red		58
3	 (dmpe)	orange	48	59
4	 (dcpe)	yellow	220	75
5	 (bpy)	copper-red	147	90
6	 (dad)	dark-blue	194	95
7	 (tmeda)	dark-red	179	64

[a] Mixture of two isomers, not separated.

3.3° and may be compared with 3.9 (1)° in Ni[P(*o*-$MeC_6H_4O)_3]_2(CH_2{=}CHCN)$,[31] 6.6 (11)° in Ni[P(*o*-$MeC_4H_6O)_3]_2(C_2H_4)$,[31] and 12° in $Ni(PPh_3)_2(C_2H_4)$.[32] The Ni···O(1) distance (3.318 (4) Å) suggests that the ester group does not interact with the metal atom. This is in accordance with observations made on other nickel complexes coordinated with α,β-unsaturated carboxylic acid derivatives.[33] However, in the case of a ferracyclopentane derivative, such an interaction has been established by X-ray analysis.[34] The Ni···S = 3.074 (4) and Ni···O(4) = 3.104(4) Å distances are slightly shorter than the sum of the van der Waals radii[35] (Ni···S = ca. 3.43 Å, Ni···O = ca. 3.15 Å), indicating an unusually short nonbonding interaction.

The conformational preferences in d^{10} nickel tris(olefin) complexes have been the subject of theoretical investigations.[36] These show that a planar (in-plane) arrangement of the double bonds is electronically favored over an upright structure. Because of the steric constraints of the cyclic cod ligand, its two double bonds cannot adopt an "in-plane" arrangement. The sma double bond, however, retains the conformation predicted by theory. The result is a new type of complex geometry that we call perpen-

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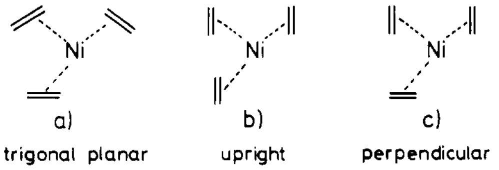

a) trigonal planar b) upright c) perpendicular

Figure 4. Conformational preferences in nickel tris(olefin) complexes.

dicular (see Figure 4c). It is worth noting that in solution at elevated temperatures the sma rotates (vide supra).

Ligand Substitution Reactions. The crystallographic data suggest that the cyclooctadiene unit in Ni(cod)(sma) is only weakly bound to the metal. In order to investigate whether a better donor would replace the cod ligand, we performed a number of ligand substitution reactions (cf. eq 2 and Table VI). All reactions occur within minutes

$$\underset{\mathbf{1}}{\mathrm{Ni(cod)(sma)}} + \mathrm{L_2} \xrightarrow[-\mathrm{cod}]{} \underset{\mathbf{2-7}}{\mathrm{NiL_2(sma)}} \qquad (2)$$

at room temperature or below. Even with 1,6-dimethylcycloocta-1,5-diene (dime-cod), the weakest of the donors, a quantitative substitution could be achieved under mild conditions. The product is formed as red needles. NMR spectroscopic investigations revealed the product to be a mixture of two isomers. Recrystallization from Et_2O resulted in an enrichment of one of them (89/11 ratio). The olefinic cyclooctadiene protons of the main isomer resonate at δ 6.02 and 5.10. The reaction of Ni(cod)(sma) with dmpe yielded compound **3** as analytically pure yellow crystals. The ^{31}P NMR spectrum recorded at −60 °C consists of an AB pattern with a J(P–P) coupling of 37.2 Hz, which is typical for NiL_2(olefin) complexes.[37]

Addition of dcpe to Ni(cod)(sma) gave yellow crystals of compound **4**. Its ^{31}P NMR spectrum consists of an AB pattern, even at room temperature (J(P–P) = 29.8 Hz). The ^1H NMR spectrum provides additional information concerning the molecular structure. Both sets of olefinic protons show two different P couplings, suggesting that the complex adopts a trigonal-planar conformation with two phosphorus atoms and the C=C double bond lying in the coordination plane of the nickel atom.

Nitrogen donors should also be excellent candidates for ligand substitution reactions of the described type. 2,2′-Bipyridine (bpy), 1,4-diaza-buta-1,3-dienylbis(2,6-xylene) (dad), and ethylenebis(dimethylamine) (tmeda) were investigated. Adding bpy to Ni(cod)(sma) gave compound **5** immediately at room temperature. It could be isolated as a hemitetrahydrofuranate in almost quantitative yield. The copper-red crystals of Ni(bpy)(sma) are sparingly soluble in nearly all common organic solvents, except *N,N*-dimethylformamide. In the ^1H NMR spectrum of **5** the α and α' hydrogen atoms of bipyridine give rise to two well-separated resonances at δ 9.51 and 8.78, which strongly indicates a trigonal-planar nickel geometry.

Replacement of cyclooctadiene by dad gave dark blue crystals of compound **6**. A low-field shift of the methine protons of dad is observed in the ^1H NMR spectrum of Ni(dad)(sma), indicating the diazadiene to be coordinated to nickel through the nitrogen lone pairs rather than through the C=N double bonds.[38]

A quantitative replacement of cyclooctadiene could also be achieved with tmeda, the strongest donor in this series. It occurred under mild conditions, giving dark red crystals of compound **7**. The upfield shift of the sma olefinic protons in the ^1H NMR spectrum of **7** (δ 2.59 and 2.05) may be a reflection of the electron-donating ability of tmeda.

The substitution reactions described above gave only 16-electron complexes. Ligand addition to form 18-electron products was not observed. To determine whether this is in fact the case the following NMR experiment was undertaken: Ni(cod)(sma) and PMe_3 (1/1 ratio) were mixed in benzene-d_6 and the ^1H NMR spectrum of this mixture was recorded immediately. The spectrum obtained was not that of $Ni(PMe_3)$(cod)(sma) but rather that of a 1/1 mixture of Ni(cod)(sma) and $Ni(PMe_3)_2$(sma). It appears that a 18-electron complex is not stable under these conditions. This is in accord with chemical expectations.[1]

We were also interested to know whether sma can be displaced by more electron-deficient olefins.[40] It is known that the SO_2 group has a −I effect of 1.0 ± 0.2 eV while its conjugative effect is only about 0.2–0.3 eV.[39] Maleic anhydride should therefore be a possible candidate. We tested this by reacting Ni(cod)(sma) with 1 equiv of maleic anhydride (mah) at −20 °C. This reaction gave Ni(cod)(mah) in 86% isolated yield (eq 3). Ni(cod)(mah)

$$\underset{\mathbf{1}}{\mathrm{Ni(cod)(sma)}} + \mathrm{mah} \xrightarrow{\mathrm{THF,\ -20\ ^\circ C}} \underset{\mathbf{8}}{\mathrm{Ni(cod)(mah)}} + \mathrm{sma} \qquad (3)$$

mah = maleic anhydride

has already been mentioned in the literature.[1] On the other hand, sma is more electron deficient than dimethyl fumarate (fdm) and should replace the latter. Thus we prepared (cycloocta-1,5-diene)(dimethyl fumarate)nickel [Ni(cod)(fdm)] and treated it with sma (eq 4). Ligand

$$\underset{\mathbf{9}}{\mathrm{Ni(cod)(fdm)}} + \mathrm{sma} \xrightarrow{\mathrm{THF,\ 22\ ^\circ C}} \underset{\mathbf{1}}{\mathrm{Ni(cod)(sma)}} + \mathrm{fdm} \qquad (4)$$

fdm = dimethyl fumarate

replacement indeed took place, and the title compound was isolated in 96% yield. Hence the coordinating ability of activated olefins increases in the order fdm < sma < mah. With strained olefins such as norbornen, norbornadiene, methylenecyclopropane, or 3,3-dimethylcyclopropene no stoichiometric reactions were observed and in all cases, the unchanged nickel complex was recovered at room temperature. At elevated temperatures, however, catalytic cyclodimerization reactions of the strained olefins occurred.

Acknowledgment. We are grateful to C.-I. K.-H. Claus for X-ray data collection and to Dr. R. Benn and Dr. A. Rufinska for providing fully assigned high-field NMR spectra. Dr. D. Henneberg and Dr. K. Seevogel kindly provided mass and IR spectra, respectively.

Registry No. 1, 91158-50-8; 2, 91158-51-9; 3, 91158-52-0; 4, 91158-53-1; 5, 91158-54-2; 6, 91158-55-3; 7, 91158-56-4; 8, 91158-57-5; 9, 91158-58-6; $Ni(PMe_3)_2$(sma), 91158-59-7; $Ni(sma)_2$, 91158-60-0; Ni(cdt), 39330-67-1; $Ni(cod)_2$, 1295-35-8.

Supplementary Material Available: Table I, summary of crystal data, tables of positional and thermal parameters, and a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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