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Articles

α,*β*-Unsaturated Carbonyl Compounds as Hard/Soft Chelating Ligands in Methyl Nickel Phenolates and the Structure of *trans*-Methyl-2-(3-phenyl-2,3-η^2-propenoyl)phenolatobis(trimethylphosphine)nickel(II)

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Phenolato functions of chalcone type compounds may replace both methoxo bridges in dinuclear methyl nickel complexes without utilizing the aldehyde functions. Cleavage of phenolato-bridged nickel(II) centers in square planar coordination geometry by addition of trimethylphosphine affords mononuclear methylnickel complexes of coordination number five. The trimethylphosphine-supported trigonal bipyramidal methyl nickel(II) complex has a hard/soft chelating ligand with a phenolato oxygen atom and a π-coordinated olefin functional group. The chemical reactivity of complexes with these novel hard/soft chelating ligands remains to be clarified.

Introduction

α,*β*-Unsaturated carbonyl compounds are useful reagents in organic synthesis. Few studies on the coordination chemistry of these multifunctional ligands have been published. When they are coordinated to transition metals, we expect several bonding modes of these ligands (Figure 1).

The coordination of cinnamate at cobalt(II) was studied,[1] showing a π-olefin bonding mode (form **a**), without formation of a chelated complex. Dicarbonyl (η^4-cinnamaldehyde)triphenylphosphineiron(0) was shown to attain coordination type **b**.[2] No complex exhibiting the coordination mode **c** has been reported so far.

Natarajan[3] obtained metal complexes (M = Co(II), Ni(II), Cu(II)) with α,*β*-unsaturated carbonyl ligands through ring-opening in the presence of pyridine or water as supporting ligands. The metal coordination occurs through a carbonyl oxygen atom and a phenolato oxygen atom. The observed interaction without utilizing the olefin function was believed to be due to the six-membered chelate ring.

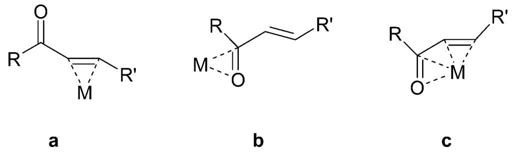

Figure 1. Coordination alternatives of α,*β*-unsaturated carbonyl ligands.

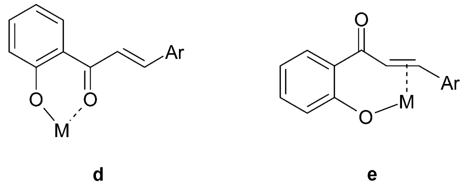

Figure 2. Coordination of chalcone ligands.

Ligands of the chalcone type can provide not only (O, O)-coordination (Figure 2, **d**) as in Natarajan's work but also phenolato-π-olefin coordination (Figure 2, **e**). In this interaction the carbon−carbon double bond π-coordinates to the metal center. This type of bonding was confirmed by Li with an indirect method.[5] Reaction of a hydrido(acyl)phenolatocobalt(III) complex with ethynyltrimethylsilane in THF afforded a π-olefin(enolato)cobalt(I) complex, which was identified by X-ray diffraction (eq 1). It was proposed that the vinyl complex after insertion is hydrolyzed.[6] The last step consists of

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(1) Hammerschmitt, B. I. Doctoral Thesis, Technische Hochschule Darmstadt, 1991.

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(6) Klein, H.-F.; Li, X.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch.* **2000**, *55b*, 707.

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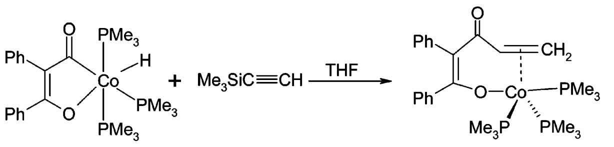
a reductive elimination at the cobalt(III) center. The coordination number is reduced from 6 to 5, and an α,β-unsaturated carbonyl compound is formed as chelating ligand. The coordination geometry is depicted in Figure 2, **e**.



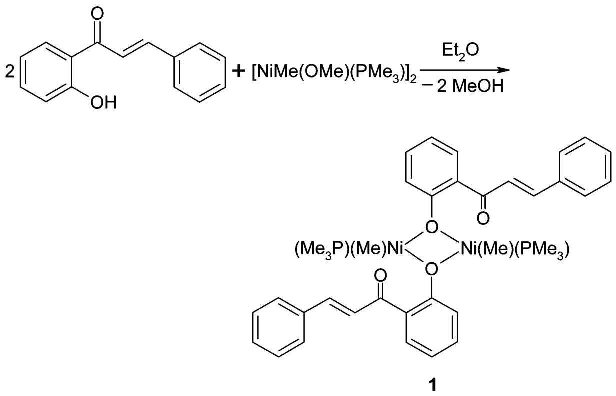
(1)

π-Coordination with an olefinic fragment on a nickel(II) center is rare. Brookhart and co-workers reported their studies on olefin polymerization with diimine Ni(II) and Pd(II) catalysts.[7] Mechanistic and theoretical work for these catalytic polymerization reactions shows that the π-interaction between the olefin fragment and the nickel(II) center is a decisive step for the polymerization.[8] These Ni(II) and Pd(II) diimine based catalysts have emerged as promising alternatives to both Ziegler−Natta systems and metallocene catalysts for olefin polymerization.

Previously we reported on the influence of hard/soft chelating ligands on the reactivity of a metal center.[9] Here we investigate the effect that a hard/soft chelating ligand exerts on a methylmetal function. Methyl(phenolato)nickel(II) complexes containing a π-coordinated olefinic function were prepared. *trans*-Methyl-2-(3-phenyl-2,3-η^2-propenoyl)phenolatobis(trimethylphosphine)nickel(II) **2** was characterized by single-crystal X-ray diffraction.

Results and Discussion

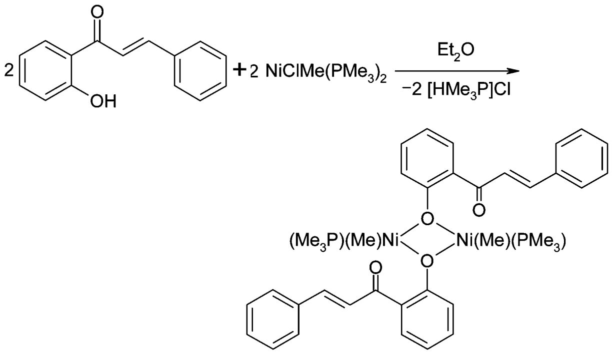
As expected of dinuclear, O-bridged methyl(methoxo)nickel(II) compounds, [NiMe(OMe)(PMe$_3$)]$_2$ reacts with substituted salicylaldehyde and enolated malondialdehyde derivatives,[10,11] while 1-(2-hydroxyphenyl)-3-phenyl-2-propenone reacts with [NiMe(OMe)(PMe$_3$)]$_2$ in diethyl ether according to eq 2 to afford bis[μ-2-oxo-(3-phenyl-2-propenone)-1-phenolato]bis[methyl(trimethylphosphine)nickel(II)], **1**.



(2)

1

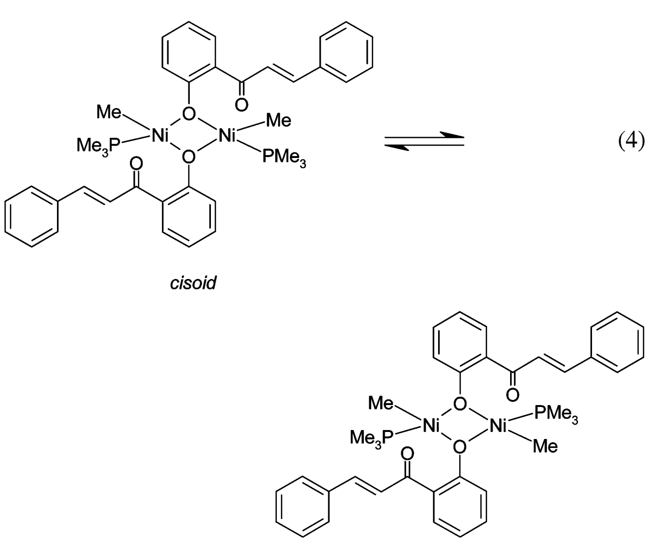
Complex **1** can also be obtained through reaction of 1-(2-hydroxyphenyl)-3-phenyl-2-propenone with NiClMe(PMe$_3$)$_2$,[12] with elimination of trimethylphosphonium chloride (eq 3). The yields are 34% and 19%, respectively.



(3)

1

Complex **1** in solution forms two isomers with *cisoid* and *transoid* configuration (eq 4). The proportion of these two configurations can be determined utilizing the signal intensity of the Ni-CH$_3$ group and trimethylphosphine ligands in the ^{1}H NMR spectra. Solvents of different polarity can shift the equilibrium concentrations of isomers. The proportion in d_6-acetone at 296 K is 1:1 (*cisoid:transoid*), while in d_8-THF it changes to 1:2. In ^{31}P NMR experiments a solvent shift of resonances was noticed. In d_6-acetone two singlets at 0.28 and 1.12 ppm were found, while in d_8-THF these singlets were moved to 0.52 and 1.42 ppm, respectively.



(4)

cisoid

transoid

A dark red solution of the dinuclear methylnickel complex **1** in diethyl ether when combined with molar equivalent amounts of trimethylphosphine at 213 K

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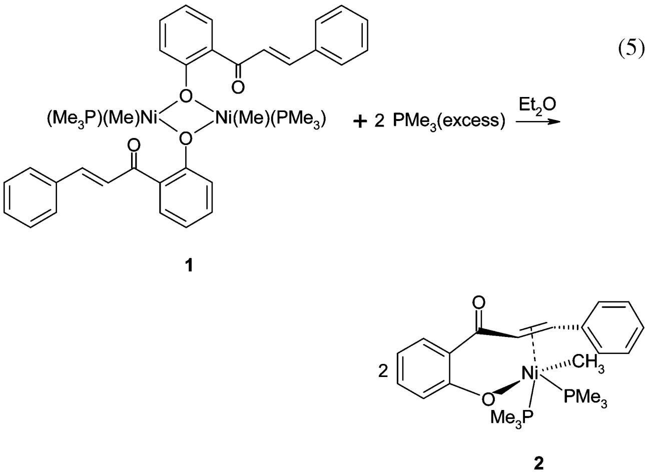
Table 1. Selected ^{1}H NMR Data (δ/ppm, J/Hz) of Complex 2 at Lower Temperatures

		296 K	233 K	223 K	213 K
olefin-C*H*	δ	3.58 (s)	3.53 (s)	3.51 (s)	3.49 (s)
		5.91 (s)	5.03 (s)	5.00 (d)	4.95 (d)
	^3J(HH)			5.6	5.6
PCH_3	δ	1.22 (d)	1.13 (d)	1.20 (t′)	1.16 (t′)
	^2J(PH)	6.4	7.0		
	$\lvert ^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})\rvert$			8.9	9.7
NCH_3	δ	−0.44 (s)	−0.36 (t)	−0.35 (t)	−0.34 (t)
	^3J(PH)		10.4	11.1	11.0

forms scarlet cubic crystals with 58% yield. From these observations it was evident that the dinuclear complex **1** is cleaved into the mononuclear methylnickel complex **2** (eq 5). The coordination of the olefinic fragment is achieved by addition of an extra trimethylphosphine ligand. At 296 K the signals of the olefinic protons were observed as two broad singlets at 3.58 and 5.91 ppm. In comparison with the resonance of the uncoordinated olefin ligand at 7.9 ppm, these protons experience a coordination shift to higher field. ^{1}H NMR measurements at lower temperatures (Table 1) confirmed this observation. While all chemical shifts were recorded at higher field with lower temperatures, those of olefinic protons were especially large. At 223 and 213 K the singlets were split into doublets with coupling constants ^3J(HH) = 5.6 Hz, which could not be resolved at higher temperature due to exchange broadening.

(5)



From a diethyl ether solution complex **2** crystallized at 245 K as red cubes, which were suitable for X-ray diffraction. The nickel is found in a trigonal bipyramidal coordination (Figure 3). Two trimethylphosphine ligands are held at relatively long distances, Ni−P(1) = 2.2443(10) Å and Ni−P(2) = 2.2477(10) Å, and the olefin function C(8)−C(9) lies in the equatorial plane NiP(1)-P(2). Methyl carbon and phenolato oxygen atoms are oriented in the axial direction. In comparison with an isoelectronic cobalt(I) complex[5,6] the distance of 1.982(3) Å between nickel and the center of the C=C bond is significantly larger than that of the cobalt complex (1.899(8) Å). The olefinic double bond, C(8)−C(9) = 1.393(4) Å, lies close to the average value (1.40 Å) for olefin ligands in transition metal complexes.[13] Since the C=C bond in the nickel complex is shorter than that of the cobalt(I) complex (1.451(11) Å), the π-coordination in complex **2** appears to be weaker. The packing does not show significant intermolecular contacts.

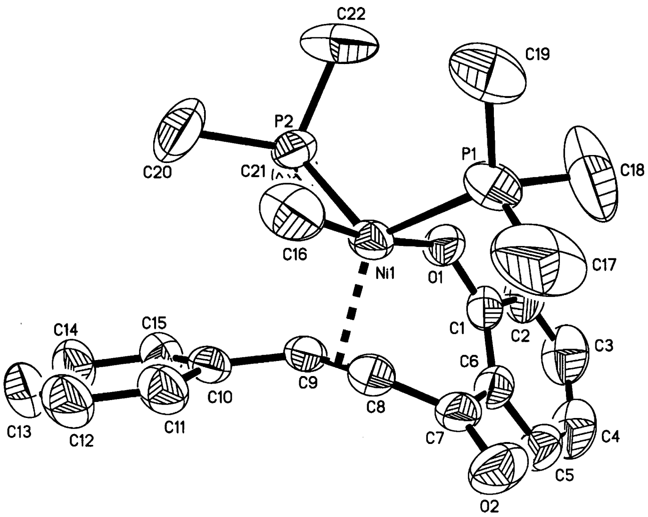
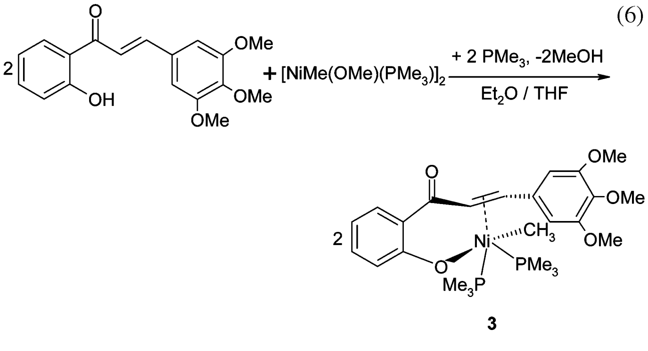


Figure 3. Molecular structure[14] of complex **2** and selected bond parameters (Å, deg): Ni−O(1) 1.9359 (18), Ni−C(8) 2.075(3), Ni−C(9) 2.127(2), Ni−C(16) 1.975(3), Ni−P(1) 2.2443(10), Ni−P(2) 2.2477(10), C(6)−C(7) 1.473(4), C(7)−C(8) 1.468(4), C(8)−C(9) 1.393(4), C(9)−C(10) 1.476(3), C(1)−C(6) 1.412(4), C(1)−O(1) 1.308(3); O(1)−Ni−C(16) 170.77(12), O(1)−Ni−C(9) 91.22(9), C(16)−Ni−C(9) 97.19(12), O(1)−Ni−P(1) 88.88(6), C(8)−Ni−P(1) 104.76(8), C(16)−Ni−P(2) 89.87(12), P(1)−Ni−P(2) 117.99(4), C(7)−C(8)−C(9) 123.2(2), O(1)−Ni−C(8) 95.05(9), C(16)−Ni−C(8) 93.89(13), C(8)−Ni−C(9) 38.69(10), C(16)−Ni−P(1) 86.65(12), O(1)−Ni−P(2) 85.11(6), C(9)−Ni−P(2) 98.57(7), C(8)−C(9)−C(10) 125.9(2).

In a one-pot synthesis (eq 6) starting from [NiMe(OMe)(PMe$_3$)]$_2$ and 1-(2-hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)-2-propenone in the presence of excess trimethylphosphine in diethyl ether/THF (1:1) the methyl(phenolato)nickel(II) complex **3** was obtained in 64% yield.

(6)



Conclusion

Phenolato functions of chalcone type compounds may replace both methoxo bridges in dinuclear methyl nickel complexes without utilizing the aldehyde functions. Cleavage of phenolato-bridged nickel(II) centers in square planar coordination geometry by addition of trimethylphosphine affords mononuclear methylnickel complexes of coordination number 5. The trimethylphosphine-supported trigonal bipyramidal methyl nickel(II) complex has a hard/soft chelating ligand with a phenolato oxygen atom and a π-coordinated olefin functional group. The chemical reactivity of complexes

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with these novel hard/soft chelating ligands remains to be clarified.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. 1-(2-Hydroxyphenyl)-3-phenyl-2-propenone (Aldrich) was used without purification. 1-(2-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)-2-propenone,[15] $[\mathrm{NiMe(OMe)(PMe_3)}]_2$,[12]and $\mathrm{NiMeCl(PMe_3)_2}$[12] were synthesized according to literature procedures. Microanalyses were carried out by Kolbe, Microanalytical Laboratory, Mülheim (FRG). Infrared spectra (4000−400 $\mathrm{cm^{-1}}$), as obtained from Nujol mulls between KBr windows, were recorded on a Perkin-Elmer, type 397, spectrophotometer. ^{1}H NMR spectra were obtained from a Bruker 300 spectrometer equipped with a low-temperature unit that was calibrated with a standard methanol sample. Melting points were measured in capillaries sealed under argon and are uncorrected.

Preparation of Bis(*μ*-2-(3-phenylpropenoyl)phenolato)bis(methyl(trimethylphosphine)nickel(II)) (1). Method a: A sample of 1.17 g (3.23 mmol) of $[\mathrm{NiMe(OMe)(PMe_3)}]_2$ and 1.45 g (6.46 mmol) of 1-(2-hydroxyphenyl)-3-phenyl-2-propenone in 60 mL of diethyl ether changed color from yellow-brown to dark red. After 20 h at 293 K the volatiles were removed in vacuo and the residue was extracted with pentane over a glass-sinter disk (G3). Freezing at 246 K afforded 0.83 g of dark red sticks (34%). Method b: 1.60 g (6.47 mmol) of $\mathrm{NiClMe(PMe_3)_2}$ and 1.45 g (6.46 mmol) of 1-(2-hydroxyphenyl)-3-phenyl-2-propenone in 60 mL of diethyl ether at 213 K gave an orange-red solution. Warming to room temperature and removing the volatiles afforded a red-brown residue, which was extracted with pentane. At 246 K 0.75 g of dark red crystals (19%) were generated. Dec > 375 K. Anal. Calcd for $\mathrm{C_{38}H_{46}Ni_2O_4P_2}$ (745.8): C, 61.17; H, 6.21; P, 8.30. Found: C, 61.13; H, 6.34; P, 8.35. IR (Nujol mull, 2000−1600 $\mathrm{cm^{-1}}$): 1626 (sst), 1609 (st) ν(C=O). ^{1}H NMR (300 MHz, d_6-acetone, 296 K, ppm, *cisoid*:*transoid* = 1:1): δ $\mathrm{NiC}H_3$ −0.59 (d, *transoid*-6H, ^3J(PH) = 4.0 Hz); −0.48 (d, *cisoid*-6H, ^3J(PH) = 6.8 Hz); $\mathrm{PC}H_3$, 1.32 (d, *transoid*-18H, ^2J(PH) = 10.4 Hz), 1.39 (d, *cisoid*-18H, ^2J(PH) = 9.8 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 6.44 (m, 4H); 6.58 (dd, 2H, ^3J(HH) = 8.8 Hz, ^4J(HH) = 1.3 Hz); 6.73 (dd, 2H, ^3J(PH) = 8.8 Hz. ^4J(PH) = 1.7 Hz); $\mathrm{C}H_{\mathrm{benzol}}$, 7.22−7.80 (m, 36 H). ^{1}H NMR (300 MHz, d_8-THF, 296 K, ppm, *cisoid*:*transoid* = 1:2): δ $\mathrm{NiC}H_3$ −0.59 (s, *transoid*-6H); −0.48 (d, *cisoid*-6H, ^3J(PH) = 6.7 Hz); $\mathrm{PC}H_3$, 1.30 (d, *transoid*-18H, ^2J(PH) = 10.3 Hz), 1.37 (d, *cisoid*-18H, ^2J(PH) = 9.9 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 6.37 (dt, 4H, ^3J(HH) = 7.8 Hz, ^4J(HH) = 0.89 Hz); 6.54 (d, 2H, ^3J(HH) = 8.7 Hz); 6.72 (d, 2H, ^3J(PH) = 8.7 Hz); $\mathrm{C}H_{\mathrm{benzol}}$, 7.10−7.95 (m, 36 H). ^{13}C NMR (50.3 MHz, d_6-acetone, 296 K, ppm): $\mathrm{Ni}C\mathrm{H_3}$, −10.30 s, −9.45 s; $\mathrm{P}C\mathrm{H_3}$, 13.53 (d, ^1J(PC) = 29.0 Hz), 13.0 (d, ^1J(PC) = 30.1 Hz); *C* and *C*H, 102,9 s, 114.3 s, 121.6 s, 123.2 s, 124.1 s, 126.1 s, 126.2 s, 129.0 s, 129.2 s, 129.8 s, 130.1 s, 130.7 s, 131.1 s, 131.3 s, 135.6 s, 136.5 s, 142.3 s, 142.7 s; *C*-O, 172.5 s, 172.7 s; *C*=O, 184.6 s, 185.3 s. ^{31}P NMR: (81.0 MHz, 296 K, ppm): in d_6-acetone, $P\mathrm{CH_3}$, 0.28 s, 1.12 s; in d_8-THF, $P\mathrm{CH_3}$, 0.52 s, 1.42 s.

***trans*-Methyl-2-(3-phenyl-2,3-η^2-propenoyl)phenolatobis(trimethylphosphine)nickel(II) (2).** To a clear solution of 1.10 g (1.47 mmol) of complex **1** in 60 mL of diethyl ether was condensed trimethylphosphine (1.0 g, 12.5 mmol), causing a pale red color. After 2 h at room temperature the mixture was filtered. This filtrate at 246 K afforded 0.77 g of scarlet cubes (58%). Dec > 376 K. Anal. Calcd for $\mathrm{C_{22}H_{32}NiO_2P_2}$ (449.1): C, 58.83; H, 7.18; P, 13.79. Found: C, 58.79; H, 7.35; P, 13.71. IR (Nujol mull, 2000−1500 $\mathrm{cm^{-1}}$): 1601 (sst), 1591 (st) ν(C=O); 1541 (m), 1500 s, ν(C=C). ^{1}H NMR (300 MHz, d_6-acetone, ppm): δ, 296 K, $\mathrm{NiC}H_3$ −0.44 (s, 3H); $\mathrm{PC}H_3$, 1.22 (d, 18H, ^2J(PH) = 6.4 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 3.58 (s, 1H); 5.91 (s, br, 1H); $\mathrm{C}H_{\mathrm{benzol}}$, 6.28−7.44 (m, 9 H). 233 K, $\mathrm{NiC}H_3$ −0.36 (t, 3H, ^3J(PH) = 10.4 Hz); $\mathrm{PC}H_3$, 1.13 (d, 18H, ^2J(PH) = 7.0 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 3.53 (s, 1H); 5.03 (s, 1H); $\mathrm{C}H_{\mathrm{benzol}}$, 6.25−7.44 (m, 9 H). 223 K, $\mathrm{NiC}H_3$ −0.35 (t, 3H, ^3J(PH) = 11.1 Hz); $\mathrm{PC}H_3$, 1.20 (t′, 18H, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})|$ = 8.9 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 3.51 (s, 1H); 5.00 (d, 1H, ^3J(HH) = 5.6 Hz); $\mathrm{C}H_{\mathrm{benzol}}$, 6.25−7.29 (m, 9 H). 213 K, $\mathrm{NiC}H_3$ −0.34 (t, 3H, ^3J(PH) = 11.0 Hz); $\mathrm{PC}H_3$, 1.16 (t′, 18H, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})|$ = 9.7 Hz); $\mathrm{C}H_{\mathrm{Olefin}}$, 3.49 (s, 1H); 4.95 (d, 1H, ^3J(HH) = 5.6 Hz); $\mathrm{C}H_{\mathrm{benzol}}$, 6.25−7.27 (m, 9 H). ^{13}C NMR (50.3 MHz, d_6-acetone, 296 K, ppm): $\mathrm{Ni}C\mathrm{H_3}$, −3.36 s, $\mathrm{P}C\mathrm{H_3}$, 13.63 s, *C* and *C*H, 113,3 s, 124.8 s, 128.1 s, 128.7 s, 129.4 s, 130.7 s, 134.0 s, 139.1 s. ^{31}P NMR (81.0 MHz, d_6-acetone, ppm): $P\mathrm{CH_3}$, 296 K, −8.53 s; 213 K, 3.24 s.

***trans*-Methyl-2-(3-(3,4,5-trimethoxyphenyl)-2,3-η^2-propenoyl)phenolatobis(trimethylphosphine)nickel(II) (3).** $[\mathrm{NiMe(OMe)(PMe_3)}]_2$ (0.31 g, 0.84 mmol) and 1-(2-hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)-2-propenone (0.53 g, 1.69 mmol) in a mixture of 30 mL of diethyl ether and 30 mL of THF were stirred for 2 h at 293 K. Onto the clear solution was condensed trimethylphosphine (0.32 g, 4.21 mmol). After 16 h the volatiles were removed in vacuo and the residue was extracted with pentane over a glass-sinter disk (G3). Freezing at 246 K afforded 0.58 g of red cubes (64%). Dec > 351 K. Anal. Calcd for $\mathrm{C_{25}H_{38}NiO_5P_2}$ (539.2): C, 55.69; H, 7.10; P, 11.49. Found: C, 55.74; H, 7.03; P, 11.59. IR (Nujol mull, 2000−1500 $\mathrm{cm^{-1}}$): 1600 (sh), 1581 (sst) ν(C=O). 1544 (m), 1511 s, ν(C=C). ^{1}H NMR (300 MHz, d_8-THF, 296 K, ppm): δ, $\mathrm{NiC}H_3$ −0.50 (s, 3H); $\mathrm{PC}H_3$, 1.11 (s, 18H); *para*-$\mathrm{OC}H_3$, 3.71 (s, 3H); *meta*-$\mathrm{OC}H_3$, 3.80 (s, 6H); $\mathrm{C}H_{\mathrm{olefin}}$, 6.05 (s, br, 2H); $\mathrm{C}H_{\mathrm{benzol}}$, 6.30 (t, 1H, ^3J(HH) = 7.4 Hz), 6.49 (d, 1H, ^3J(HH) = 8.5 Hz), 6.78 (m, 2H), 7.02 (ddd, 1H, ^3J(HH) = 6.9 Hz, ^4J(HH) = 1.7 Hz), 7.50 (m, 1H). ^{13}C NMR (75.4 MHz, d_8-THF, 296 K, ppm): $\mathrm{Ni}C\mathrm{H_3}$, −6.5 s; $\mathrm{P}C\mathrm{H_3}$, 11.88 s; $\mathrm{O}C\mathrm{H_3}$, 54.5 s, 58.5; *C*H, 104.5 s, 111.3 s, 123.0 s, 128.9 s, 131.9 s, 152.7 s; *C*-O, 168.8 s. ^{31}P NMR (121.5 MHz, d_8-THF, 296 K, ppm): $P\mathrm{CH_3}$, −21.26 s.

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Supporting Information Available: Tables containing full X-ray crystallographic data for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal structure analysis of **2**: $\mathrm{C_{22}H_{32}NiO_2P_2}$, Bruker AXS P4 diffractometer, Mo Kα radiation (λ = 0.71073 Å, graphite monochromator), T = 293(2) K, crystal size 0.18 × 0.30 × 0.58 $\mathrm{mm^3}$, triclinic, space group $P\bar{1}$, a = 8.672(1) Å, b = 11.251(1) Å, c = 13.458(2) Å, α = 68.88(1)°, β = 74.54(1)°, γ = 74.89(1)°, V = 1160.6(2) Å^3, Z = 2, D_c = 1.258 g/cm^3, μ(Mo Kα) = 0.987 $\mathrm{mm^{-1}}$, F(000) = 476, 6299 reflections collected 2.1° < θ < 27.5°, absorption correction via psi-scans, min./max. transmission 0.795/0.942, 5252 independent intensities (R_{int} = 0.014), structure solution by direct and conventional Fourier methods, full-matrix least-squares refinement based on F^2 and 245 parameters, all but hydrogen atoms refined anisotropically, H atoms at idealized positions riding on their attached carbon atoms, refinement converged at R1($I > 2\sigma(I)$) = 0.043, wR2 (all data) = 0.107, S = 1.008, max. Δ/σ = 0.0001, min./max. height in final ΔF map = −0.38/0.39 e Å^{-3}. Programs for solution and refinement were from the SHELX suite.[16] Crystallographic data, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre, with deposition number CCDC-269319. Data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (e-mail: deposit@ccdc.cam.ac.uk).

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