Electronic Structure and Reactivity of Ylide Systems. 18.[1] X-ray Structure Analysis of a Bis(ylide)nickel Catalyst[†]

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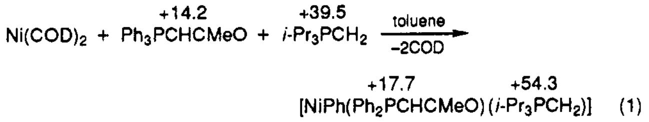
Summary: Known differences in the activity and selectivity of ylide catalysts **1** and phosphine catalysts **2** made a comparison of the structures of **1**–**3** desirable. An X-ray structure determination of $[\mathrm{NiPh(Ph_2PCHCMeO)(\textit{i}\text{-}Pr_3PCH_2)}]$ (**1a**) confirms the presence of a structurally intact C-coordinated $i\text{-}\mathrm{Pr_3PCH_2}$-ylide ligand in the trans position to the diphenylphosphino group of a $\mathrm{Ph_2PCHCMeO\text{-}P^\frown O}$ chelate. The most striking finding is a dramatic increase in the NiO bond length to 1.95 Å as a consequence of a structurally intact coordinated ylide ligand.

The bis(ylide)nickel catalysts described by us in the past few years have given synthetic access to soluble matrix polyacetylenes in a highly polar polymer matrix for the first time.[1] The specific choice of the ligands provides excellent possibilities of optimizing activity and controlling selectivity in ethylene and acetylene polymerization.[1-6] We have already reported the peculiarities in the electronic structure of ylide ligands, which become apparent in photoelectron spectra[7-9] and the spectroscopic properties of ylide complexes.[4,6,7] Figures 1 and 2 show the results of an X-ray structural analysis of **1a**, a catalyst of this type, obtained in high yield by stoichiometric reaction of [bis(cyclooctadiene)nickel(0)] with (acetylmethylene)triphenylphosphorane and methylenetriisopropylphosphorane in toluene at approximately 50 °C (eq 1; the ^{31}P NMR resonances (ppm) are listed above the compound). It crystallizes from toluene as dark yellow crystals.



$$\mathrm{Ni(COD)_2} + \overset{+14.2}{\mathrm{Ph_3PCHCMeO}} + \overset{+39.5}{i\text{-}\mathrm{Pr_3PCH_2}} \xrightarrow[-2\mathrm{COD}]{\text{toluene}} \underset{\mathbf{1a}}{[\mathrm{NiPh}\overset{+17.7}{(\mathrm{Ph_2PCHCMeO})}\overset{+54.3}{(i\text{-}\mathrm{Pr_3PCH_2})}]} \quad (1)$$

The crystal structure confirms the basic predictions of multinuclear NMR studies of the catalyst in solution,[10] i.e., the presence of a structurally intact C-coordinated $i\text{-}\mathrm{Pr_3PCH_2}$ ylide ligand in the trans position to the diphenylphosphino group of a $\mathrm{Ph_2PCHCMeO\text{-}P^\frown O}$ chelate. It also confirms that the fourth coordination site, trans to the enolate-*O*, is occupied by a phenyl group (Figures 1 and 2). The four atoms directly linked to the Ni atom (2 C, P, O) are all positioned in exactly the same plane, the maximum deviation being 0.005 Å. The nickel atom deviates 0.051 Å from this plane (below the plane in Figure 2) so the nickel coordination is virtually planar.

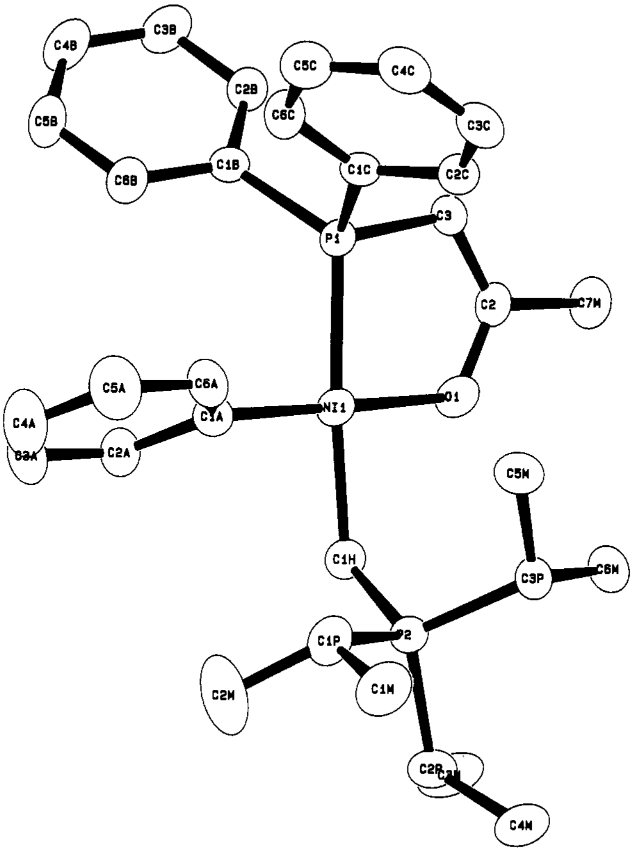
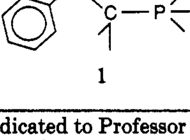


Figure 1. Molecular structure of 1a with atom numbering. The hydrogen atoms are omitted for clarity. The thermal ellipsoids enclose 30% of the electron density.

The basic structure 1 is thus related to types 2 and 3. A comparison is of interest because of the known differences in the activity and selectivity[11] of ylide 1 and phosphine catalysts 2,[12] while *cis*-$[\mathrm{Ni(P^\frown O)_2}]$ complexes of type 3 can be detected as polymerization-inactive de-



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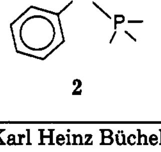

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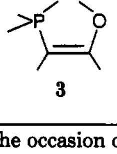

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[†] Dedicated to Professor Karl Heinz Büchel on the occasion of his 60th birthday.

(1) Part 17: Ostoja Starzewski, K. A.; Bayer, G. M. *Angew. Chem.* **1991**, *103*, 1012; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 961.

(2) Ostoja Starzewski, K. A.; Witte, J. *Angew. Chem.* **1988**, *100*, 861; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 839.

(3) Ostoja Starzewski, K. A.; Witte, J.; Reichert, K. H.; Vasiliou, G. In *Proceedings of the International Symposium on Transition Metals and Organometallics as Catalysts for Olefin Polymerization (Hamburg, 1987)*; Kaminsky, W., Sinn, H., Eds.; Springer Verlag: Heidelberg, Germany, 1988.

(4) Ostoja Starzewski, K. A.; Witte, J. In *Proceedings of the International Symposium on Transition Metal Catalyzed Polymerizations (Akron, OH, 1986)*; Quirk, R., Eds.; Cambridge University Press: New York, 1988.

(5) Ostoja Starzewski, K. A.; Witte, J. *Angew. Chem.* **1987**, *99*, 76; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 63.

(6) Ostoja Starzewski, K. A.; Witte, J. *Angew. Chem.* **1985**, *97*, 610; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599.

(7) Ostoja Starzewski, K. A.; tom Dieck, H. *Inorg. Chem.* **1979**, *18*, 3307.

(8) Ostoja Starzewski, K. A.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 8486.

(9) Ostoja Starzewski, K. A.; Richter, W.; Schmidbaur, H. *Chem. Ber.* **1976**, *109*, 473.

(10) Assignment and interpretation of the NMR spectra of **1a** are consistent with our earlier findings on the solution structure of another bis(ylide)nickel catalyst **1b**: $[\mathrm{NiPh(Ph_2PCHCPhO)(Me_3PCH_2)}]$. For a detailed discussion of **1b**, see ref 6.

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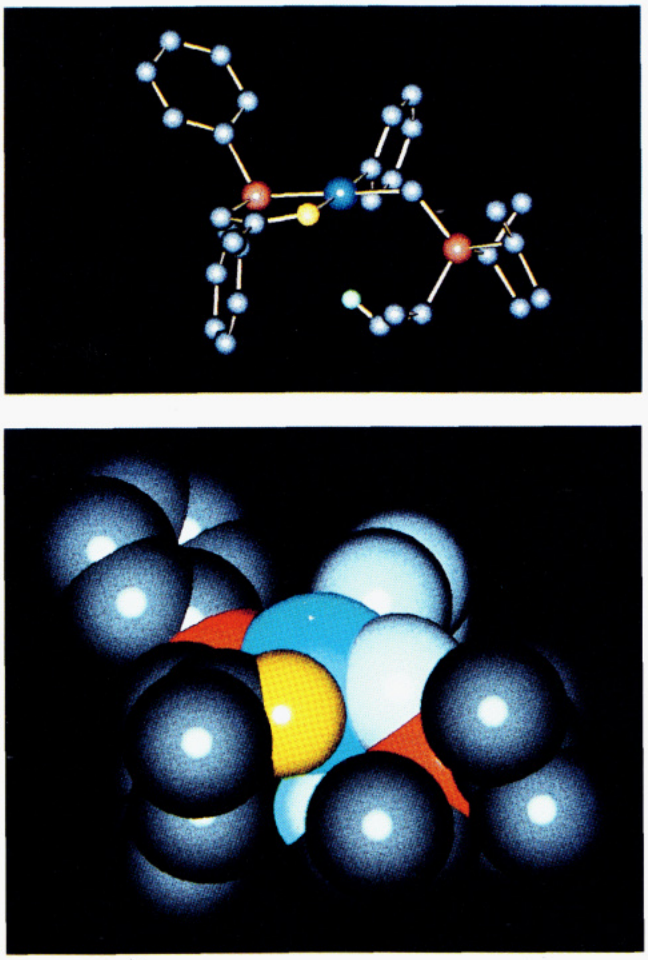

Figure 2. Molecular structure of **1a** in the crystal showing the open region above the coordination plane, providing access to the nickel center: (a, top) ball and stick model; (b, bottom) space-filling model (Ni = blue, P = red, O = yellow, ylide-C_α–nickel and phenyl-C–nickel = light gray). For reasons of clarity, the H atoms have been omitted, with the exception of the one directly below the nickel center that is mentioned in the text.[17]

Table I. Selected Bond Lengths (Å) and Angles (deg) for 1a[a]

	Bond Lengths		
Ni(1)–P(1)	2.176 (1)	P(2)–C(1H)	1.765 (4)
Ni(1)–O(1)	1.951 (3)	P(2)–C(1P)	1.824 (5)
Ni(1)–C(1H)	1.966 (4)	P(2)–C(2P)	1.844 (5)
Ni(1)–C(1A)	1.890 (4)	P(2)–C(3P)	1.820 (5)
P(1)–C(3)	1.761 (4)	O(1)–C(2)	1.302 (5)
P(1)–C(1B)	1.822 (4)	C(2)–C(7M)	1.516 (6)
P(1)–C(1C)	1.839 (4)	C(2)–C(3)	1.358 (6)
	Bond Angles		
P(1)–Ni(1)–O(1)	85.4 (9)	C(3)–P(1)–C(1C)	106.4 (2)
P(1)–Ni(1)–C(1H)	172.6 (1)	C(1B)–P(1)–C(1C)	101.9 (2)
P(1)–Ni(1)–C(1A)	93.9 (1)	C(1H)–P(2)–C(1P)	110.1 (2)
O(1)–Ni(1)–C(1H)	87.6 (2)	C(1H)–P(2)–C(2P)	111.7 (2)
O(1)–Ni(1)–C(1A)	176.6 (2)	C(1H)–P(2)–C(3P)	111.6 (2)
C(1H)–Ni(1)–C(1A)	92.9 (2)	C(1P)–P(2)–C(2P)	108.1 (2)
Ni(1)–P(1)–C(3)	100.1 (2)	C(1P)–P(2)–C(3P)	106.9 (2)
Ni(1)–P(1)–C(1B)	120.5 (1)	C(2P)–P(2)–C(3P)	108.3 (2)
Ni(1)–P(1)–C(1C)	118.7 (1)	Ni(1)–O(1)–C(2)	118.4 (3)
C(3)–P(1)–C(1B)	108.4 (2)	Ni(1)–C(1H)–P(2)	120.1 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table II. Comparison of Bond Lengths (Å) in (PC_2ONi) Metallacycles

	d(PC)	*d*(CC)	*d*(CO)	*d*(NiP)	*d*(NiO)
[$NiPh(Ph_2PCHCMeO)$-(Pr_3PCH_2)] (**1a**)	1.761	1.358	1.302	2.176	1.951
[$NiPh(Ph_2PCHCPhO)$-(Ph_3P)] (**2a**)[12a]	1.769	1.365	1.313	2.168	1.914
[$Ni(Ph_2PCHCPhO)_2$] (**3a**)[12b]	1.760	1.356	1.318	2.168	1.885

composition products of **1** and **2**, e.g. after completed polymerization.[13]

Peculiarities of the "intact" ylide ligand are the Ni–C–P angle of 120.1° (Table I), which is unusually wide for a tetrahedral carbon, and a P–C_α bond length of 1.765 Å, which seems short in comparison with the 1.82–1.84 Å of the single bonds PC(isopropyl) and PC(phenyl) and falls into a range that is rather more typical for stabilized ylides.[14] This suggests that the ($P^+ - C^-$) bond polarity typical of free ylides basically remains in the coordinated state. This receives further support from the position of the $^{13}C_\alpha$ NMR resonance at −6 ppm relative to the tetramethylsilane standard! The bond to the nickel center Ni–C(ylide) is 1.970 Å, which is long compared to the Ni–C(phenyl) bond length of 1.890 Å (Table I). However, both distances are still within the known range of nickel alkyl and nickel phenyl complexes.[15] The P atom of the intact ylide ligand is located 1.50 Å below the nickel coordination plane, with which the (Ni–C–P) plane forms an angle of 84.6°. Through this conformation one i-propyl methyl group from "underneath" comes almost within interaction distance at *d*(Ni- - -H) = 2.55 Å. At the same time, the region above the nickel is wide open, for example, to monomer coordination (Figure 2). The phenyl ring directly linked to the Ni atom is rotated 66.6° from the nickel coordination plane. The Ni–C(phenyl) bond (1.890 Å) is even shorter than in the phosphine complex **2a**, where it is 1.893 Å. This nickel–phenyl moiety is particularly interesting because insertion of a monomer molecule into this bond is regarded as the first step in the catalytic cycle.[16] It is perhaps worth mentioning here that in ethene oligomerization/polymerization reactions, catalysts of type **1** frequently have somewhat higher activation temperatures than equally substituted derivatives of type **2** (e.g. 80 °C/50 °C).

While the four centers of the phosphinoenolate ligand in **1a** have somewhat shorter bond lengths than in the phosphine complex **2a**, it is striking that the P–Ni bond *trans* to the ylide is only slightly shorter than in **2a** and **3a**, while the O–Ni bond in the *cis* position is considerably longer (Table II). As the O center moves stepwise away from the nickel (**3a** → **2a** → **1a**), the C–O bond becomes

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[11] With the same substitution pattern, catalysts of type **1** are more active than those of type **2**. Under identical polymerization conditions, a higher degree of polymerization is obtained with **1** than with **2**; see also refs 1–6.

[12] (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 493; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polym. Sci. Polym. Chem.* **1987**, *25*, 1989.

[13] From **1a** in a form of red crystals: mass spectrum, *m/e* = 540 (mol peak), ^{31}P NMR (C_6D_6, H_3PO_4), δ = 26.8 ppm.

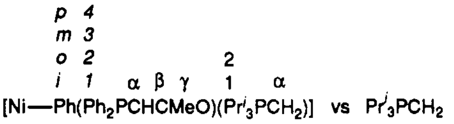
[14] Compare e.g. the following values. $d(PC_\alpha)$ = 1.736 Å in the stabilized ylide $Ph_3PC(Cl)CPhO$: Stephens, F. S. *J. Chem. Soc.* **1965**, 5640, 5658. $d(PC_\alpha)$ = 1.661 Å in the nonstabilized ylide Ph_3PCH_2: Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350. $d(PC_\alpha)$ values in the metallacycles of **1a**, **2a**, and **3a** are given in Table II.

[15] Jolly, P. W.; Wilke, G. In *Organometallic Chemistry-The Organic Chemistry of Nickel*; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic Press: New York, London, 1974; Vol. 1, p 497 and literature cited therein.

[16] GC/MS studies on reaction solutions of ethylene with catalysts of type **1** confirm the presence of styrene.

[17] Fortran program (SCHAKAL 88B) for the graphic representation of molecular and crystallographic models by: Keller, E. Kristallographisches Institut der Universität, D-7800 Freiburg, Germany.

Table III. ^{13}C NMR Data for Methylenetriisopropylphosphorane and for Bis(ylide)nickel Catalyst 1a, the Latter Being Fully Assigned to a Structurally Intact Coordinated Ylide Ligand, a Nickel-Bound Phenyl Group, and a P͡O Chelating Group[a]



$[Ni{-}Ph(Ph_2PCHCMeO)(Pr^i_3PCH_2)]$ vs $Pr^i_3PCH_2$

	intact ylide ligand			free ylide		
	C-2	C-1	C-α	C-2	C-1	C-α
δ(^{13}C)	+17.2	+22.5	−6.4	+17.4	+23.8	−19.8
$^1J(^{31}P^{13}C)$		45	17		49	90
$^2J(^{31}P^{13}C)$	n.r.		48	n.r.		
$^1J(^{13}C^1H)$	129	129	127	128	125	149

	Ni–Ph group			
	C-*i*	C-*o*	C-*m*	C-*p*
δ(^{13}C)	+156.8	+125.2	+128.3	+120.4
$^nJ(^{31}P^{13}C)$	32	n.r.	n.r.	n.r.
$^1J(^{13}C^1H)$		154	148	157

	P͡O chelating ligand						
	C-*4*	C-*3*	C-2	C-*1*	C-α	C-β	C-γ
δ(^{13}C)	+139.3	+127.8	+133.1	+137.0	+78.2	+186.0	+23.8
$^nJ(^{31}P^{13}C)$	4	n.r.	10	44	53	25	12
$^1J(^{13}C^1H)$	162	159	161		165		125

[a] *J* values are in Hz.

Table IV. Crystal Data for [NiPh(Ph$_2$PCHCMeO)(*i*-Pr$_3$PCH$_2$)]

molecular formula	$C_{31}H_{42}OP_2Ni$
fw	551.34
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	12.042 (1)
b, Å	16.210 (1)
c, Å	15.339 (1)
β, deg	100.76 (1)
V, Å^3	2941.6
Z	4
d(calc), g·cm^{-3}	1.245
μ, cm^{-1}	21.3
no. of obsd refls *m*	2688
no. of params refined	485
R,[a] %	3.8
final shift/error	0.13
CAD4 four-circle diffractometer	Cu Kα
T, K	297

[a] $R = \sum|K|F_o| - |F_c||/\sum K|F_o|$.

shorter. **1a** is thus approaching a borderline situation, defined by an ylide with a metal complex substituent on the phosphorus: $L_2Ni–Ph_2PCHCMeO$. Due to the presence of the intact ylide ligand, the structural consequences of the interaction of fragment orbitals of the rearranged ylide with energetically destabilized basis functions of the nickel become apparent. Should dynamic processes in the catalytic cycle require a change in the position of the O ligand, structure 1 would provide the best starting point. A (Ni- - -O) dissociative process would generate an extremely electron-rich, coordinatively unsaturated Ni center as a transition state.

Table V. Positional Parameters and *B* Values and Their Estimated Standard Deviations for [NiPh(Ph$_2$PCHCMeO)(*i*-Pr$_3$PCH$_2$)]

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ni(1)	0.35102 (6)	0.77378 (4)	0.17104 (4)	3.33 (1)
P(1)	0.53063 (9)	0.78415 (7)	0.16893 (7)	3.35 (2)
P(2)	0.08669 (9)	0.81671 (7)	0.10345 (7)	3.42 (2)
O(1)	0.3721 (2)	0.8735 (2)	0.2436 (2)	4.18 (7)
C(1H)	0.1925 (3)	0.7739 (3)	0.1863 (3)	3.84 (9)
C(2)	0.4719 (4)	0.9073 (3)	0.2599 (3)	3.8 (1)
C(7M)	0.4805 (4)	0.9864 (3)	0.3133 (3)	5.1 (1)
C(3)	0.5625 (4)	0.8758 (3)	0.2302 (3)	3.8 (1)
C(1A)	0.3342 (4)	0.6736 (3)	0.1068 (3)	3.7 (1)
C(2A)	0.3126 (4)	0.6004 (3)	0.1477 (3)	4.6 (1)
C(3A)	0.3048 (5)	0.5252 (3)	0.1049 (4)	6.3 (1)
C(4A)	0.3173 (6)	0.5215 (3)	0.0179 (4)	7.6 (2)
C(5A)	0.3379 (5)	0.5925 (4)	−0.0250 (3)	6.9 (2)
C(6A)	0.3473 (4)	0.6673 (3)	0.0191 (3)	4.5 (1)
C(1B)	0.6287 (3)	0.7043 (3)	0.2189 (3)	3.47 (9)
C(2B)	0.7231 (4)	0.7252 (3)	0.2810 (3)	4.4 (1)
C(3B)	0.8020 (4)	0.6660 (3)	0.3175 (3)	5.5 (1)
C(4B)	0.7856 (4)	0.5857 (3)	0.2930 (3)	5.4 (1)
C(5B)	0.6910 (4)	0.5638 (3)	0.2332 (3)	5.3 (1)
C(6B)	0.6130 (4)	0.6221 (3)	0.1959 (3)	4.7 (1)
C(1C)	0.5751 (3)	0.8008 (3)	0.0619 (3)	3.43 (9)
C(2C)	0.5524 (4)	0.8764 (3)	0.0197 (3)	4.1 (1)
C(3C)	0.5828 (4)	0.8924 (3)	−0.0607 (3)	4.8 (1)
C(4C)	0.6362 (4)	0.8336 (3)	−0.1019 (3)	5.1 (1)
C(5C)	0.6585 (4)	0.7583 (3)	−0.0624 (3)	5.4 (1)
C(6C)	0.6279 (4)	0.7422 (3)	0.0193 (3)	4.8 (1)
C(1P)	0.0612 (4)	0.7498 (3)	0.0061 (3)	5.3 (1)
C(1M)	−0.0144 (5)	0.7861 (4)	−0.0754 (3)	6.2 (1)
C(2M)	0.0165 (7)	0.6644 (4)	0.0283 (5)	9.7 (2)
C(2P)	−0.0479 (4)	0.8296 (3)	0.1427 (3)	4.9 (1)
C(3M)	−0.0305 (4)	0.8479 (4)	0.2429 (4)	7.3 (2)
C(4M)	−0.1267 (4)	0.8955 (4)	0.0926 (3)	5.7 (1)
C(3P)	0.1289 (4)	0.9168 (3)	0.0667 (3)	3.9 (1)
C(5M)	0.2303 (4)	0.9087 (3)	0.0206 (3)	5.2 (1)
C(6M)	0.1527 (4)	0.9795 (3)	0.1428 (3)	5.0 (1)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Experimental Section

All manipulations were performed under rigorous exclusion of air and water, using high-vacuum-line and Schlenk techniques. Argon was passed through a surface Cr(II) catalyst before using it as inert gas. Solvents were appropriately dried and distilled in an argon atmosphere, and all glassware was oven dried, prior to use.

Preparation of 1a. Under an argon atmosphere, a 500-mL Schlenk flask was charged with 8.25 g (30 mmol) of yellow crystalline bis(cyclooctadiene)nickel(0) followed by 9.54 g (30 mmol) of white crystalline (acetylmethylene)triphenylphosphorane. Next, 250 mL of dry, argon-saturated toluene was added. To the magnetically stirred suspension, 5.74 g (33 mmol) of methylenetriisopropylphosphorane was injected using a syringe.

The reaction mixture was stirred at 50–60 °C for 4 h. The homogeneous dark yellow brown solution was filtered through a Celite layer and the volatiles were removed in vacuo. The residue was redissolved at 50–60 °C in ca. 50 mL of toluene. Hexane was added until a beginning cloudiness remained, and the solution was slowly cooled, first to room temperature and then to 5 °C. The dark yellow crystals formed were isolated by Schlenk filtration, washed with hexane, dried in vacuo, and kept under argon.

Yield: 14.8 g (~90%). Anal. Calcd for $C_{31}H_{42}OP_2Ni$: C, 67.53; H, 7.68. Found: C, 67.7; H, 7.5. ESCA: BE ($Ni2p_{3/2}$) 853.5 eV. Mass spectrum: m/e 550 (M^+ for ^{58}Ni), 507 (M − Pr), 376 (M − Pr_3PCH_2), 318 ($Ph_3PCHCMeO$), 174 (Pr_3PCH_2), 77 (Ph). ^1H NMR (C_6D_6, TMS internal): intact ylide ligand i-Pr_3PCH_2, δ +0.53 (dd, $^2J(P,H)$ = 13.1 Hz, $^3J(P,H)$ = 5.4 Hz, CH_2), +0.91 (dd, $^3J(P,H)$ = 14.4 Hz, $^3J(H,H)$ = 7.0 Hz, 6 CH_3), +1.88 (approx d-sept, $^2J(P,H)$ = 12 Hz, $^3J(H,H)$ = 7 Hz, 3 H); rearranged ylide, δ +2.10 (s, CH_3), +4.38 (d, $^2J(P,H)$ = 0.6 Hz, CH), +6.84 to +7.77 (m, 3 C_6H_5). ^{13}C NMR (C_6D_6, TMS internal) data are given in Table III. For ^{31}P NMR data, see eq 1 in the text.

Crystallographic Structure Determination for Complex 1a. A yellow crystal of **1a** (0.15 × 0.175 × 0.225 mm^3) was mounted on an Enraf-Nonius CAD4 diffractometer, equipped with graphite-monochromated Cu Kα radiation (λ = 1.54056 Å). Cell parameters were determined by a least-square refinement of angular coordinates of 22 reflections. Data were collected at room temperature by the θ–2θ scan technique. A total of 4366 independent reflections was measured in the range $10° < \theta < 60°$ ($\pm h,+k,+l$) of which 2688 with $I \geq 3\sigma(I)$ were used in the subsequent refinements. Data were corrected for absorption[18] (transmission factors: 0.998 max, 0.947 min) and Lorentz–polarization effects. Calculations were performed on a Micro VAX computer using the Enraf-Nonius structure determination package.[19] Crystal data are found in Table IV. The structure was solved by a combination of direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms isotropically. Fractional atomic coordinates of non-hydrogen atoms are given in Table V.

Registry No. **1a**, 89743-12-4; i-Pr_3PCH_2, 29218-76-6; $Ni(COD)_2$, 1295-35-8; $Ph_3PCHCMeO$, 1439-36-7.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, thermal parameters, bond lengths, bond angles, dihedral angles, and least-squares planes and a figure showing a unit cell and packing diagram (12 pages). Ordering information is given on any current masthead page.

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Cluster Building on a Bicarbide Fragment: Synthesis and Structure of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$

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Summary: Thermal reaction of the ethynediyl complex $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{\equiv}C)]$ (**1**) with diiron nonacarbonyl occurs with formation of $[Fe_2Ru_2(\mu_4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ (**2**), a cluster containing a bicarbide ligand. A structural study has shown that one of the ruthenium atoms migrates from a position where it is σ-bonded to a single ethynediyl carbon to become η^2-bonded to the ethynediyl unit. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 9.579 (5) Å, b = 24.789 (4) Å, c = 10.621 (5) Å, β = 115.02°, Z = 4, V = 2285 (2) Å^3, 2679 reflections with $I \geq 3\sigma(I)$, R = 0.049, R_w = 0.056.

Alkynes have long been known to react with metal carbonyls, particularly $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$, to give an enormous variety of interesting complexes.[1,2] Extension of this methodology to metal alkynyls (acetylides, $L_nM{-}C{\equiv}CR$) gave complexes in which the carbon–carbon triple bond is coordinated to Fe or Co, sometimes with the concomitant formation of direct M—Fe or M—Co bonds.[3-11]

Ethynediyl complexes ($L_nM{-}C{\equiv}C{-}ML_n$) comprise a relatively small but rapidly expanding group of compounds whose reactivity is little studied.[12-30] Our recent report

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