

Reactions of Chelate Ylides with Nickel(0) Complexes

Wilhelm Keim,* Arno Behr, Bert Gruber, Bernd Hoffmann,, Frank H. Kowaldt, Ulf Kürschner, Brigitte Limbäcker, and Frank P. Sistig

Institute of Technical Chemistry and Petrochemistry, Technical University Aachen, D-5100 Aachen, FRG

Received January 17, 1986

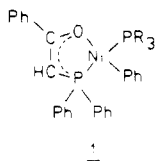
Nickel(0) complexes react with α -keto ylides of phosphorus and arsenic, $\text{Ph}_3\text{A}=\text{BC}(\text{O})\text{R}$ ($\text{A} = \text{P}, \text{As}$; $\text{B} = \text{CH}, \text{CR}', \text{N}$), yielding a variety of new nickel complexes. In this novel reaction an unusual phenyl group migration is observed. Depending on the nature of the nickel(0) complexes applied, the phenyl group migrates to the nickel, thus forming a nickel-phenyl bond, or the phenyl group migrates to the hydrocarbon ligand, thus forming the corresponding C-C-linked hydrocarbon product. The nickel-phenyl bond proved to be quite reactive toward insertion of molecules such as carbon monoxide, carbon dioxide, ethene, and tolan. When carbon monoxide and tolan were used, the corresponding nickel complexes could be isolated. Interestingly, the isolated complexes are active catalyst precursors for the oligomerization of ethene to give highly linear α -olefins.

Introduction

Chelate ligands have an unusual selectivity-controlling effect in the nickel-catalyzed oligomerization and polymerization of ethene.¹⁻³ Especially ligands containing $\overline{\text{P}}\text{O}$ chelates show a high activity and selectivity and are utilized, for instance, in the SHOP process for the manufacture of α -olefins, which is operated by Shell in two large plants.^{4,5}

It is common practice in homogeneous transition-metal catalysis to prepare organometallic model complexes, which serve as precursors to the active catalytic species. In this way it is possible to gain some understanding of the ligand requirements.

We have already reported the synthesis of complex 1 which is a very active catalyst in the SHOP process.²



Complex 1 formally can be described as consisting of two ligand units: a π, σ -coordinated chelate part, $\overline{\text{P}}\text{O}$, and a σ -coordinated nickel-carbon bond containing the fragment $(\text{R}_3\text{P})\text{Ni}-\text{Ph}$. The question arises how alterations of the two parts affect the catalytic behavior.⁶ To this end, we have attempted the synthesis of a large variety of $\overline{\text{P}}\text{O}$ chelate complexes, and this has led to novel reaction modes of α -keto ylides with nickel(0) complexes. Our results are reported in this paper.

Experimental Section

The ¹H NMR spectra were recorded at 90 MHz on a Varian Model EM 390 or at 200 MHz on a Bruker Model CXP 200 NMR spectrometer. The shifts are expressed as δ values relative to Me_4Si . The ¹³C NMR and ³¹P NMR spectra were recorded on the Bruker Model CXP 200. In ¹³C NMR spectroscopy, C_6D_6 ,

toluene-*d*₈, or acetone-*d*₆ were used as internal standards; in ³¹P NMR spectroscopy 85% phosphoric acid was used as external standard. The IR spectra were measured on a Perkin-Elmer 577 spectrophotometer using KBr pellets. Mass spectra were recorded on a Varian MAT 112 instrument combined with the Varian Spectro System MAT 188 using an ion source with a temperature of 210 °C, a pressure of 10⁻⁵ torr and an ionization energy of 70 eV. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer.

The α -keto ylides were prepared by methods described in the literature or were commercially available substances: (benzoylmethylene)triphenylphosphorane,⁷ (1-(ethoxycarbonyl)ethylidene)triphenylphosphorane (Aldrich Chemical), 4-hydroxy-6-(triphenylphosphoranylidene)cyclohexa-2,4-dien-1-one,⁸ triphenylphosphine benzoylimide,⁹ and (benzoylmethylene)triphenylarsorane.¹⁰

Synthesis of Complexes According to Eq 3. Nickel bis(1,5-cyclooctadiene), $[\text{Ni}(\text{cod})_2]$, was prepared by the method of Wilke and Bogdanović¹¹ by treating nickel(II) acetylacetonate with 1,5-cyclooctadiene and triethylaluminum. Equimolar amounts of $\text{Ni}(\text{cod})_2$, the ylide, and triphenylphosphine were allowed to react in toluene under argon at room temperature for about 24 h. After the cyclooctadiene was evaporated, the nickel complexes were crystallized from toluene/pentane mixtures.

As a typical example the synthesis of complex 5 is described in detail. $\text{Ni}(\text{cod})_2$ (4.6 g, 16.75 mmol) was dissolved in 160 mL of toluene, and solutions of 6.39 g (16.75 mmol) of triphenylphosphine benzoylimide in 650 mL of toluene and 4.40 g (16.8 mmol) of triphenylphosphine in 50 mL of toluene were added successively with stirring. After the addition of PPh_3 , a deep red color appeared. After the solution was stirred further for 24 h at room temperature and heated at 50 °C for 1 h, the solvent was distilled at 0.01 torr. In the distillate 95% of cyclooctadiene was accounted for by gas chromatography. The residue was washed with acetone, crystallized from a mixture of toluene and pentane and dried at 0.01 torr to yield 7.8 g (66%) of complex 5.

By this method complexes 1-6 could be prepared in yields between 50 and 75%. Their analytical and spectral data are summarized in Tables I-III.

Synthesis of the Benzoyl Complex 7 (See Eq 8). A suspension of 1 g (1.43 mmol) of 5 in 30 mL of a 1:2 mixture of toluene and pentane was cooled to -10 °C. Under intensive stirring carbon monoxide was bubbled through the suspension during 40 min. On cooling to -50 °C complex 7 precipitated. It was filtered, washed with pentane, and dried at 0.01 torr. Analytical and

(1) Keim, W. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 191.

(2) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 493.

(3) Keim, W.; Behr, A.; Limbäcker, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503.

(4) Peuckert, M.; Keim, W.; *Organometallics* **1983**, *2*, 594.

(5) Keim, W. *Chem.-Ing.-Tech.* **1984**, *56*, 850.

(6) The catalytic results will be forwarded in another paper.

(7) Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 43.

(8) Schönberg, A.; Michaelis, R. *Chem. Ber.* **1936**, *69*, 1080.

(9) Staudinger, H.; Hauser, H. *Helv. Chim. Acta* **1921**, *4*, 861.

(10) (a) Johnson, A. W.; Schubert, H. *J. Org. Chem.* **1970**, *35*, 2678. (b) Nesmeyanov, N. A.; Pravidina, V. V.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 1364.

(11) Bogdanović, B.; Kröner, M.; Wilke, G. *Justus Liebig's Ann. Chem.* **1966**, *699*, 1.

Table I. Analytical Data of the Isolated Nickel Chelate Complexes

complex	elemental anal. calcd (found)			mass spectra ^b	mp, °C	yield, %
	C	H	Ni			
1	75.3 (74.7)	5.1 (5.05)	8.3 (7.95)	440, 438, 303, 262, 105, 28	150	69
2	77.47 (76.3)	6.0 (5.8)	7.96 (7.09)	440, 438, 303, 262, 213, 182, 122, 105, 91, 77, 28	150	73
3	72.1 (72.2)	5.6 (5.6)	8.5 (8.4)	nd ^a	165 dec	75
4	72.97 (72.86)	4.92 (4.95)	8.50 (8.45)	370 (ylide), 262 (PPh ₃)	188 dec	61
5	73.54 (73.33)	4.99 (5.46)	8.37 (8.39)	304 (Ph ₂ PNCOPh), 262 (PPh ₃), 105 (PhCO)	180 dec	66
6	70.90 (70.90)	4.91 (4.88)	nd ^a	nd ^a	165	52
7	72.35 (72.36)	4.80 (4.84)	8.04 (8.70)	nd ^a	137	86
8	77.74 (77.40)	5.15 (5.76)	6.67 (6.63)	304 (Ph ₂ PNCOPh), 262 (PPh ₃)	145	51
9	68.53 (68.75)	5.25 (5.35)	14.56 (14.00)	401 (M ⁺), 360	145	51
10	69.11 (70.69)	5.56 (5.69)	14.07 (16.01)	415 (M ⁺), 360	130	40
11	69.11 (69.09)	5.56 (5.68)	14.07 (13.80)	415 (M ⁺), 361	127	59
12	70.30 (70.38)	5.03 (5.00)	13.74 (13.70)	428/426 (M ⁺), 362, 360, 326, 324, 286, 258, 256, 202, 200	163	nd ^a

^and = not determined. ^bCharacteristic signals.

Table II. IR and ¹H NMR Spectra of the Isolated Nickel Chelate Complexes

complex	IR data, cm ⁻¹	¹ H NMR data, δ
1	1560, 1480, 1350, 825	7.6 (12 H, m), 7.0 (20 H, m); 6.6 (3 H, m), 5.2 (1 H, s) ^b
2	1560, 1480, 1350, 825	7.6 (12 H, m), 7.1 (11 H, m), 6.82 (6 H, d, <i>J</i> = 7.5 Hz), 6.7 (3 H, m), 5.18 (1 H, s), 1.94 (9 H, s) ^b
3	1530, 1100	7.6 (12 H, m), 7.1 (18 H, m), 3.5 (2 H, l), 1.8 (3 H, t), 0.85 (3 H, t) ^b
4	1560	7.6 (12 H, m), 7.1 (15 H, m), 6.7 (3 H, m), 6.3 (3 H, m), 3.67 (1 H, s) ^b
5	1560	8.2 (2 H, m), 7.5 (10 H, m), 7.0 (20 H, m), 6.6 (3 H, m) ^b
6	1560, 1335, 1280	7.5 (12 H, m), 7.0 (20 H, m), 6.6 (3 H, m), 5.5 (1 H, s) ^b
7	1615	nd ^a
8	similar to 12	8.3–7.5 (14 H, m), 7.3–6.5 (31 H, m) ^b
9	1585, 1505	8.15 (2 H, m), 7.6 (4 H, m), 7.15 (<i>x</i> H, m), 5.1 (1 H, s), 4.75 (1 H, m), 4.19 (1 H, m), 2.86 (1 H, m), 2.37 (1 H, m), 1.28 (1 H, d) ^c
10	1585, 1505	8.15 (2 H, m), 7.6 (4 H, m), 7.15 (<i>x</i> H, m), 5.1 (1 H, s), 4.02 (1 H, m), 2.86 (1 H, m), 2.23 (1 H, m), 1.65 (3 H, s), 1.34 (1 H, m) ^c
11	1580, 1520	8.15 (2 H, m), 7.6 (4 H, m), 7.15 (<i>x</i> H, m), 5.2 (1 H, s), 4.70 (1 H, dt), 3.60 (1 H, m), 2.40 (1 H, m), 1.54 (3 H, dd), 1.31 (1 H, d, <i>J</i> = 13 Hz) ^c
12	1582, 1510	7.9–7.3 (15 H, m), 5.40 (5 H, s), 5.11 (1 H, d, <i>J</i> = 2 Hz) ^b

^and = not determined. ^bIn C₆D₆. ^cIn toluene-*d*₈.

Table III. ¹³C and ³¹P NMR Spectra of the Isolated Nickel Chelate Complexes

complex	¹³ C NMR data, δ	³¹ P NMR data, δ	
		chelate P	phosphine P
1	76.0 (methine C), 120–140 (aromatic C), 183.0 (carbonyl C)	22.3	20.8
2	21.3 (CH ₃), 77.5 (methine C), 120–140 (aromatic C), 181.8 (carbonyl C)		19.1
3	nd ^a		nd ^a
4	117–147 (aromatic C), 170–177 (carbonyl C)		22.5
5	121–147 (aromatic C), 182.6 (carbonyl C)	71.2	22.0
6	79.7 (methine C), 121–141 (aromatic C), 179.0 (carbonyl C)		² <i>J</i> _{pp} = 285 Hz
7	126–139 (aromatic C), 180.50 and 181.95 (carbonyl C)	65.8	23.08
8	124.4, 125.3, 126.0, 127–135, 142.3, 144.1, 145.9, 146.8, 151.9 (dd), 181.5 (dd)	69.6	21.7
9	42.5 (s), 70.6 (d), 77.3 (d), 112.5 (s), 136.8 (d), 139.6 (d), 183.2 (d)	25.4	21.5
10	23.6 (s), 43.4 (s), 68.8 (d), 77.4 (d), 125.8 (s), 136.1 (d), 137.1 (d), 140.5 (d), 184.6 (d)	26.5	
11	17.3 (s), 38.0 (s), 77.2 (d), 87.2 (d), 111.9 (s), 135.8 (d), 138.6 (d), 183.1 (d)	22.9	
12	79.9 (d), 92.04 (s), 127–138, 209.8 (s)	34.3	

^and = not determined.

spectral data for 7 are given in Tables I–III.

Synthesis of the Tolan Insertion Product 8 (See Eq 9).

Compound 5 (1.4 g, 2 mmol) was dissolved in 15 mL of toluene and the solution cooled to 0 °C. A solution of 0.36 g (2 mmol) of diphenylacetylene (tolane) in 5 mL of toluene was added dropwise. After the solution was stirred for 12 h at room temperature, the solvent was evaporated at 0.01 torr, and the residue was filtered through silica. Cooling to -25 °C yielded red crystals of complex 8 which were washed with cold diethyl ether and dried in vacuo. Analytical and spectral data for 8 are shown in Tables I–III.

Synthesis of Complexes According to Eq 4. Bis(η³-allyl)-nickel,¹² bis(η³-methallyl)nickel,¹³ and bis(η³-crotyl)nickel¹³ were

prepared by literature methods; dicyclopentadienylnickel is available from Alfa Chemicals.

In a typical example, the synthesis of complex 9 is described in detail. Ph₃PCHCOPh (22.8 g, 60 mmol) was dissolved in a mixture of 500 mL of toluene and 250 mL of tetrahydrofuran and the solution cooled to -20 °C. Bis(η³-allyl)nickel (9.8 g, 70 mmol) was dissolved at -50 °C in 50 mL of toluene and added to the solution of the ligand. The orange-red mixture was allowed to warm to room temperature and then heated at 50 °C for 1.5 h. Small amounts of nickel metal were filtered. After evaporation at 25 °C and 0.01 torr the allylbenzene in the distillate was analyzed by GLC. The residue was dissolved in toluene and the solution heated to 40 °C. Small amounts of *n*-heptane were added

(12) Bogdanović, B. Ph.D. Thesis, RWTH Aachen, 1962.

(13) Keim, W. Ph.D. Thesis, RWTH Aachen, 1963.

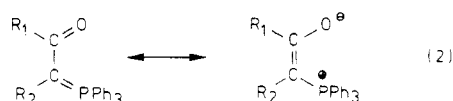
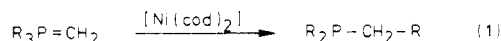
until crystallization started. After 24 h the crystals of complex 9 were filtered, washed with cold diethyl ether, and dried in vacuo (12.5 g, 31 mmol, 51% yield based on the ylide).

By this method complexes 9–12 were prepared in good yields. The analytical and spectral data for the complexes 9–12 are summarized in Tables I–III.

Results and Discussion

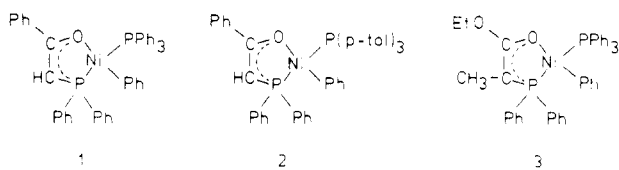
Phosphorus ylides are ligands which form stable complexes with virtually every metal of the periodic table. Normally the ylide is coordinated by various possible bonding modes. In some cases, however, rearrangements of the ylide are known, as, for instance, in eq 1.¹⁴

α -Keto ylides are interesting ligands because they can function as chelate ligands possessing a hard and a soft donor group in one molecule. Spectroscopic data support the following resonance hybrids.¹⁵



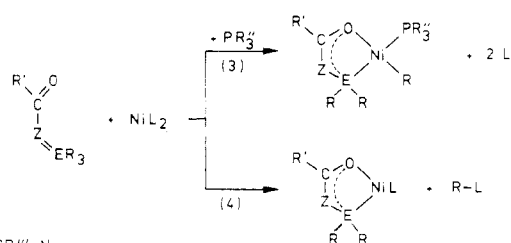
The reaction of α -keto ylides with NiL_2 ($L = 1,5$ -cyclooctadiene, η^3 -allyl, η^3 -crotyl, η^3 -methallyl, η^5 -cyclopentadienyl) proceeds by two distinct pathways as shown in Scheme I. In both, the phosphorus-carbon bond is cleaved and the phenyl group migrates. In eq 3 a new nickel-phenyl bond is formed by migration of the phenyl group to the nickel atom. In eq 4 the phenyl group migrates to one of the hydrocarbon ligands, giving the phenylhydrocarbon (RL). Whether pathway 3 or 4 is followed depends on the nature of the ligand L, the π -bonded olefin (1,5-cod), and the η^3 - or η^5 -carbon-bonded species.

Reaction of α -Keto Ylides with π -Bonded Nickel Complexes (Eq 3). (Benzoylmethylene)triphenylphosphoranes (in the presence of PPh_3 or $P(p\text{-tol})_3$) react with $Ni(1,5\text{-cod})_2$ to give complexes 1–3. The structure



of complex 1 was confirmed by X-ray diffraction, showing a square-planar arrangement of the ligand.² Distances and angles of the planar PC_2ONi ring suggest a delocalized electron system in the chelate ligand. Besides $Ni(1,5\text{-cod})_2$, also $Ni(PPh_3)_4$ can be used in the preparation of 1 and 3. For a demonstration of the general applicability of this new reaction and for a study of the effect of selected changes

Scheme I



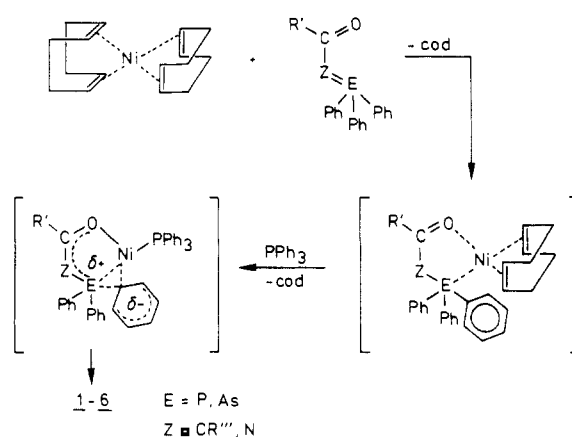
Z = CR''', N

E = P, As

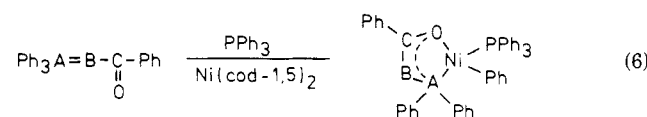
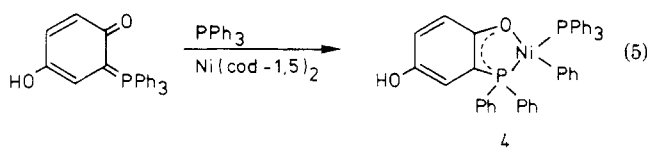
R = phenyl

L = cod-1,5, C₃H₅, C₄H₇, C₅H₅

Scheme II



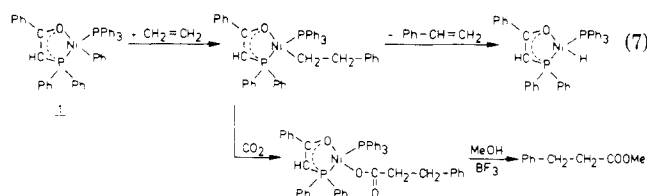
of the ligand in the catalytic ethene oligomerization reaction, complexes 4–6 were prepared according to eq 5 and 6. The structure of 6, confirmed by X-ray analysis,³ is very similar to that of complex 1. However, the square-planar coordination of nickel is slightly tilted toward tetrahedral coordination, as seen from the P–Ni–As angle of 167.5°. Also, the Ni–P distance (2.208 Å) in the position trans to arsenic is evidently shorter than that in complex 1 (2.230 Å).



	A	B
5	P	N
6	As	CH

The migration of the phenyl ring from phosphorus or arsenic, respectively, to nickel mechanistically is assumed to occur by way of an E–C–Ni three-membered ring as shown in Scheme II.

The nickel-phenyl bond of complexes 1–6 is quite reactive, and a variety of insertions are possible. For instance, ethene inserts to give styrene according to eq 7.



All attempts to isolate the assumed intermediates $L_nNiCH_2CH_2Ph$ or L_nNiH have failed so far. Therefore, in a number of experiments it was attempted to isolate a nickel hydride complex by treating 1 with hydrogen. Although quantitative formation of benzene could be

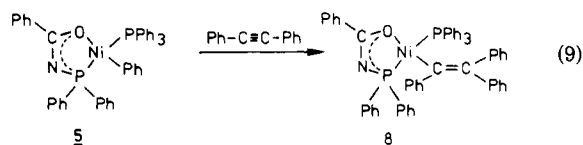
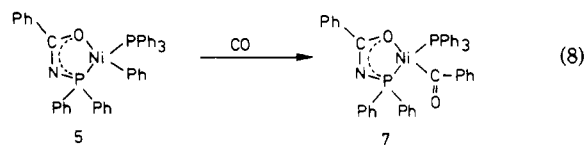
(14) Heydenreich, F. Ph.D. Thesis, Ruhr-Universität Bochum, 1971.

(15) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley-Interscience: New York, 1972; Vol. 3.

(16) U. Klabunde and S. J. Ittel of Du Pont isolated similar CO insertion products and determined the structure by X-ray analysis, thus confirming also structure 7.

confirmed, no nickel hydride complex could be isolated from the black reaction product, which was found to be soluble in polar solvents such as dimethyl sulfoxide.

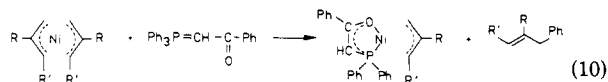
The insertions of CO (eq 8) and tolane were more successful (eq 9). Complex 7 could be isolated in high yield and characterized.¹⁶ To confirm the composition of 7 by chemical means, it was treated with methanol to give methyl benzoate and, in another experiment, with methyl iodide to give acetophenone.



Complex 8 also could be characterized by ¹H, ³¹P, and ¹³C NMR, IR, and MS spectroscopy. Chemical evidence for the Ni-vinyl group is based on the reaction with HCl, which gave triphenylethylene in high yields. Interestingly, both complexes 7 and 8 oligomerize ethene to α -olefins of >99% linearity.¹⁷

As we have reported previously, the nickel-phenyl bond in complex 1 also reacts with carbon dioxide and, concomitantly, with ethene/CO₂ yielding hydrocinnamic acid methyl ester¹⁸ (eq 7).

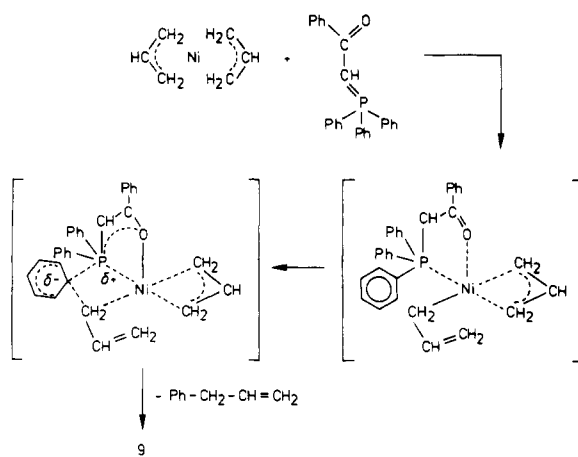
Reaction of α -Keto Ylides with η^3 - and η^5 -Bound Nickel Complexes (Eq 4). Bis(η^3 -allyl)nickel complexes react with (benzoylmethylene)triphenylphosphorane according to eq 10, yielding complexes 9–11. Interestingly,



	R	R'
9	H	H
10	CH ₃	H
11	H	CH ₃

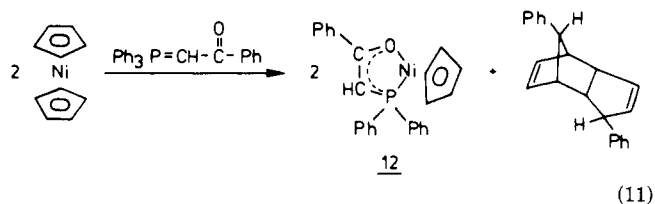
in these cases the phenyl group attacks one η^3 -allylic group giving the corresponding phenyl-substituted derivatives 3-phenyl-propene, 2-methyl-3-phenyl-propene, 4-phenyl-

Scheme III



2-butene, and 3-phenyl-butene. To account for the reaction products, a mechanism (Scheme III), which is similar to the one discussed above in Scheme II, is proposed. In this mechanism one η^3 -allyl group rearranges to a η^1 -allyl group, thus enabling the coordination of the ylide in a chelate mode. One phenyl group migrates to the η^1 -bound allyl group with a C-C linkage to give PhCH₂CH=CH₂ under concomitant formation of complex 9, for instance.

Interestingly, η^5 -cyclopentadienyl groups also undergo an identical reaction as shown in eq 11. Complex 12 could



be isolated and characterized. The concomitant formation of diphenyldicyclopentadiene results from Diels-Alder dimerization of the phenylcyclopentadiene originating from the attack of the migrating phenyl group on the coordinated cyclopentadienyl ligand.

Acknowledgment. We wish to thank the Deutsche Forschungsgemeinschaft and the Ministerium für Wissenschaft und Forschung des Landes NRW for supporting this work. We also thank Dr. W. Meltzow for carrying out the GC work, W. Falter for the GC/MS data, and M. Sistig and B. Dederichs for the NMR data. A generous gift of nickel bis(acetylacetonate) by the Dynamit Nobel AG/Troisdorf is gratefully acknowledged.

(17) Kürschner, U. Ph.D. Thesis, RWTH Aachen, 1985.

(18) Behr, A.; Keim, W.; Thelen, G. *J. Organomet. Chem.* **1983**, *249*, C38.