Reactivity of 1-Aza-4-oxa-1,3-butadienes (α-Imino Ketones) toward Diorganozinc Reagents: Regio- and Chemoselective Transfer of Organo Groups in the $ZnR_2/R^1N{=}C(R^2)C(R^3){=}O$ System and X-ray Structure of the Organozinc Enolate $[EtZn(Et)(t\text{-}Bu)NC(H){=}C(Me)O]_2$

M. Robert P. van Vliet,[1a] Gerard van Koten,*[1a] Paul Buysingh,[1a] Johann T. B. H. Jastrzebski,[1a] and Anthony L. Spek[1b]

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

Received May 30, 1986

The 1:1 reaction of ZnR_2 with α-imino ketones $[R^1N{=}C(R^2)C(R^3){=}O]$ leads to quantitative formation of dinuclear $[RZn(R)(R^1)NC(R^2){=}C(R^3)O]_2$ (1) (for R = primary and secondary alkyls) and $[RZn(R^1)N{=}C(R^2)C(R^3,R)O]_2$ (2) (for R = aryl, methyl, and tertiary alkyl). An X-ray structure determination of $[EtZn(Et)(t\text{-}Bu)NC(H){=}C(Me)O]_2$ (**1a**) has established the dinuclear structure that consists of a N,O-chelate coordinated $[Et(t\text{-}Bu)NC(H){=}C(Me)O]^-$ monoanionic ligand and a central four-membered Zn_2O_2 ring formed by intermolecular Zn–O coordination. The Zn atoms are tetrahedrally surrounded by two O atoms, one N atom, and one C atom. Crystals of **1a** are triclinic, space group $P\bar{1}$, with cell constants a = 7.57 (1) Å, b = 8.82 (2) Å, c = 11.14 (1) Å, α = 102.6 (1)°, β = 91.8 (1)°, γ = 114.4 (2)°, and Z = 1. The structure was refined to a final R of 0.089 with 1051 reflections. Product formation in the ZnR_2/α-imino ketone system depends on the nature of the R group that migrates from Zn to the NCCO skeleton. Different radical activity of R (for R = Et, *i*-Pr, *t*-Bu, and Bz) as generated in the 1:1 complex, with the ligand bonded in the N,O-chelate coordination mode (see A in Scheme II), is the predominant factor for the discrimination between imino N-addition (for R• = Et, *i*-Pr, and Bz; 20%) and carbonyl C-addition (R• = *t*-Bu and Bz; 80%). For R = Me and *p*-tolyl alternative routes involving a N-monodentate coordination mode and/or heterolytic activation may also account for the exclusive formation of carbonyl C-addition products.

Introduction

Reactions of organoaluminum, -copper, -lithium, -magnesium, and -zinc compounds with substrates containing α,β-unsaturated organic systems, X=C—C=Y, are of great importance in organic synthesis.[2] Recently renewed interest has been shown in the mechanistic aspects of these reactions.[3]

The chemistry of α-diimines, RN=CHCH=NR (R-DAB), has received much attention in our laboratory.[4] We found that contrary to the undirected product formation of R-DAB with Grignard and organolithium reagents, very selective transfer of the organo groups from organozinc or -aluminum compounds to the R-DAB diimine skeleton occurred.[5] These studies led to the development of novel synthetic routes for the synthesis of highly substituted *cis*-1,2-diaminoethene and 1,2-diamino- and 1-imino-2-aminoethane compounds.

An interesting aspect of the R-DAB/ZnR_2 system is the detailed mechanistic information that could be obtained through the isolation and characterization of (dia- and paramagnetic) organozinc intermediates from these reactions. Pertinent to the subject of this paper are the results summarized in Scheme I that show clearly the influence of the nature of the R group in the organozinc reagent on the product formation. The chelate coordination in A is the main feature of the observed reaction pathway. In the case of R = alkyl this chelate coordination triggers subsequent inner-sphere electron transfer to intermediate B. Depending on the nature of the radical R either reaction of R• with the solvent (formation of the persistent radical C) *or* further reduction of the ligand in the RZn(R-DAB)• radical by reaction with R• occurs (formation of the carbon- (F) and/or nitrogen- (E) alkylated products).[6]

We have extented these investigations to reactions of organozinc and -aluminum reagents with molecules containing the N=C—C=O moiety since such substrates can be attractive starting materials for the synthesis of complex organic skeletons containing two different heteroatoms (N and O) in the α-position. It has been shown that α-imino ketones, in reactions with lithium aluminum hydride, behave as ambident electrophiles, the carbonyl and imino groupings being respectively the hard and the soft sites

(1) (a) University of Amsterdam. (b) University of Utrecht.

(2) (a) Mauze, B.; Miginiac, M. *Bull. Soc. Chim. Fr.* **1973**, 1078. (b) Posner, G H. *Org. Reac. (N.Y.)* **1972**, *19*, 1. (c) Bergman, E. D.; Ginsburg, D.; Rappo, R. *Org. React. (N.Y.)* **1959**, *10*, 179. (d) Eicher, T. *The Chemistry of Carbonyl Compounds*; Patai, S., Ed.; Interscience: New York, 1966; p 624–631, 662–678.

(3) (a) Casey, C. P.; Casa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236. (b) Lipshutz, B. H. *Tetrahedron Lett.* **1983**, *24*, 127.

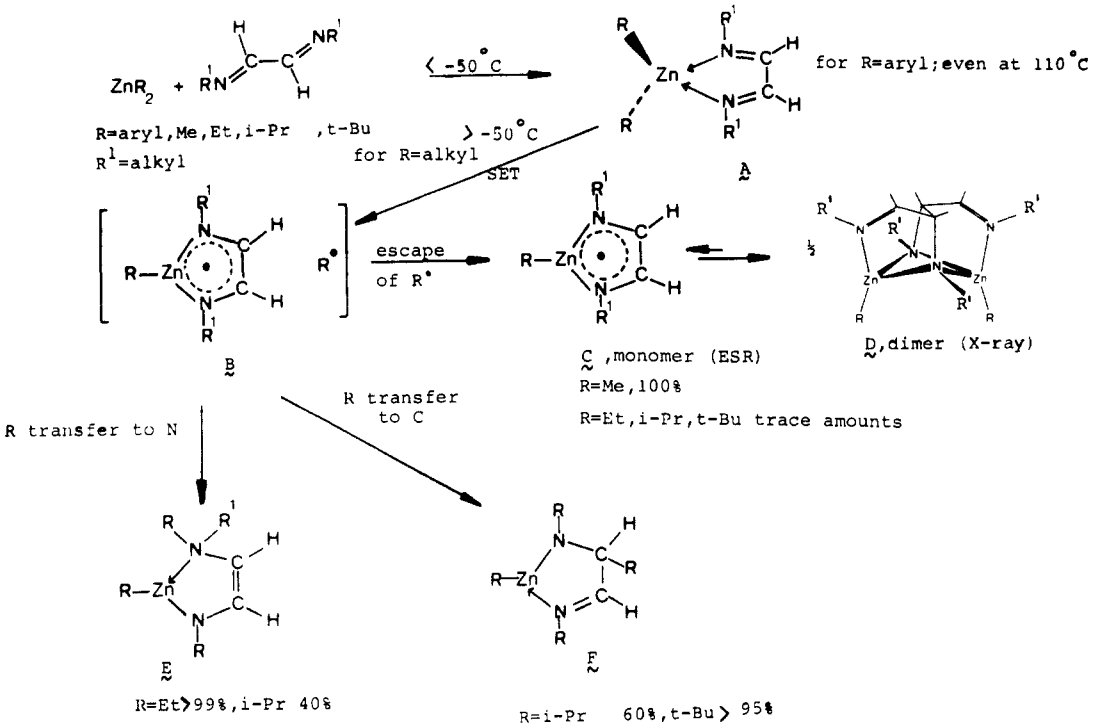
(4) (a) van Koten, G.; Vrieze, K. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 129 and references therein. (b) van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, *250*, 49 and references therein.

(5) (a) Klerks, J. M.; Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1982**, *224*, 107. (b) Klerks, J. M.; Stufkens, D. J.; van Koten, G.; Vrieze K. *J. Organomet. Chem.* **1979**, *181*, 271. (c) Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K., unpublished results.

(6) (a) Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K., to be submitted for publication. (b) Ashby, E. C.; Wieseman, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 189. (c) Rau, H.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1967**, *335*, 253. (d) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *9*, 1. (e) Noltes, J. G.; Van den Hurk, J. W. G. *J. Organomet. Chem.* **1965**, *3*, 222.

0276-7333/87/2306-0537$01.50/0

Scheme I. Proposed Mechanism Explaining All Products Formed in the Reactions of ZnR_2 with R^1-DAB[a]



[a] In addition equimolar amounts of alkane RH and alkene R(−H) were produced. The SET character of the reactions was demonstrated by the presence of trace amounts of stable persistent organozinc radicals C, which are in equilibrium with their diamagnetic dimers D (X-ray for R = Et and the imine side is pyridyl).[4b,5,28]

of the reacting system.[7] These chromophores seem to react as isolated entities. It is therefore interesting to observe that the α-imino ketones are very reactive toward dialkylzinc compounds, whereas the isolated imine (e.g., in Schiff bases) or carbonyl groupings (e.g., in ketones) react only slowly or not at all.[8] The questions then arise: in which conformation (planar trans, anti, or nonplanar gauche) does the α-imino ketone react with organometallic reagents and whether the nature of the initial complexation influences the type of products formed.[9] With regard to the question of the initial complexation, two extreme situations have to be considered: i, the formation of a complex similar to A in Scheme I with a chelate-bonded, almost flat N=C—C=O skeleton, or ii, the formation of a complex with a monodentate O- or N-bonded α-imino ketone with a nonplanar gauche conformation of the N=C—C=O skeleton. Recently, we isolated complexes of α-imino ketones with the AlR_3, $ZnCl_2$, and $PtCl_2(PR_3)$ moieties containing the α-imino ketone in either one of these coordination modes.[23,24]

In this work the above questions are explored with special emphasis on the influence of the nature of the R group in the ZnR_2 reagent on the reaction course. Rather than studying the organic products obtained after hydrolysis of the reaction mixtures, we have isolated and characterized the final organozinc products. An X-ray structure determination of the compound originating from the reaction of $ZnEt_2$ with *t*-BuN=CHC(Me)=O is reported.[10]

Experimental Section

General Data. All reactions were carried out under dry, oxygen-free nitrogen. Solvents were carefully dried and distilled before use.

The pure ZnR_2 compounds (R = *p*-tolyl, methyl, ethyl, *n*-butyl, isobutyl, isopropyl, *tert*-butyl, and benzyl) were synthesized and isolated according to published methods.[11]

The α-imino ketones $R^1N{=}C(R^2)C(R^3){=}O$ with R^1 = *t*-Bu or $EtMe_2C$, R^2 = H, and R^3 = Me as well as with R^1 = Me and R^2 = R^3 = Ph were prepared as described in the literature.[12] The other α-imino ketones used, i.e., L_1, R^1 = *t*-Bu, R^2 = H, and R^3 = Ph, and L_2, R^1 = *i*-Pr, R^2 = H, and R^3 = Ph, were synthesized starting from phenylglyoxal monohydrate and the corresponding primary amine, following similar procedures.[12a] Yield: L_1, 50%; L_2, 30%. ^1H NMR ($CDCl_3$, room temperature, Me_4Si, δ): L_1, 1.26 (s, 9 H), 7.60 (m, 5 H), 7.90 (s, 1 H); L_2, 1.24 (d, 6 H), 3.47 (sept, 1 H), 7.34 (s, 1 H), 7.63 (m, 5 H). ^{13}C NMR ($CDCl_3$, room temperature, Me_4Si, δ): L_1, 28.4 (q), 58.9 (s, *t*-Bu), 127.9 130.2 133.2, 134.4 (Ph), 153.5 (d, N=*C*), 191.4 (s, *C*=O). The latter compound decomposes at room temperature, $t_{1/2}$ = 30 min.[12c]

Syntheses of the Complexes. The course of the reactions leading to the organozinc compounds 1 and 2 appeared to be

(7) (a) Fonseca, J.; Martines-Carrera, S.; Garcia-Blanco, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2643. (b) Krow, G. R.; Rodebaugh, R.; Carmosin, R.; Figures, W.; Panella, H.; De Vilaris, G.; Grippi, M. *J. Am. Chem. Soc.* **1973**, *95*, 5273. (c) Krow, G. R.; Johnson, C.; Boyle, M. *Tetrahedron Lett.* **1971**, 1978. (d) Carcia-Ruano, J. L.; Henao, M. A.; Molina, D.; Peres-Ossorio, R.; Plumet, J. *Tetrahedron Lett.* 1979, *33*, 3123. (e) Alcaide, B.; Fernandez de la Pradilla, R.; Lopez-Mardomingo, C.; Pérez-Ossorio, R.; Plumet, J. *J. Org. Chem.* **1981**, *46*, 3234.

(8) (a) Coates, G. E.; Ridley, D. *J. Chem. Soc. A* **1966**, 1064. (b) Pattison, J.; Wade, K. *J. Chem. Soc. A* **1968**, 57.

(9) (a) Alcaide, B.; Lopes-Mardomingo, C.; Perez-Ossorio, R.; Plumet, J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1649. (b) Fonseca, J.; Martinez-Carrera, S.; Garcia-Blanco, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 3421.

(10) van Vliet, M. R. P.; Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K.; Spek, A. L. *J. Organomet. Chem.* **1983**, *251*, C17.

(11) (a) $ZnMe_2$: Galyer, A. L.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 253. (b) $ZnEt_2$: Alfa Products. (c) Zn-*i*-Pr_2: Rathke, M. W.; Yu, H. *J. Org. Chem.* **1972**, *37*, 1732. (d) Zn-*n*-Bu_2: Le Goff, E. *J. Org. Chem.* **1964**, *29*, 2048. (e) Zn-*i*-Bu_2: Lardicci, L.; Lucarini, L. *Ann. Chim. (Rome)* **1964**, *54*, 1233. (f) Zn-*t*-Bu_2: Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1975**, 1162. (g) Zn-*p*-$tolyl_2$: Kocheskov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *3*, 582. (h) $ZnBz_2$: Weissig, V.; Beckhaus, R.; Banasiak, U.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1980**, *467*, 61.

(12) (a) van der Poel, H.; van Koten, G. *Synth. Comm.* **1978**, *8*, 305. (b) Wheatley, W. B.; Fitzgibbon, W. E.; Cheney, L. C. *J. Org. Chem.* **1953**, *18*, 1564. (c) McKay, W. R.; Proctor, G. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2435.

independent of the solvents used; i.e., in either *n*-hexane, toluene, or diethyl ether essentially the same products were obtained. Correct elemental analytical and molecular weight data were obtained for all isolated compounds.[13]

Syntheses of $[RZn(R)(R^1)NC(R^2)=C(R^3)O]_2$ (1a–g). Addition of a solution of ZnR_2 (R = Et, *n*-Bu, *i*-Bu, or *i*-Pr) in hexane (10 mL, 1 M) to a solution of an equimolar amount of the α-imino ketone, likewise in hexane (100 mL) at −100 °C, resulted in the almost quantitative formation of the organozinc complex **1** (checked by ^1H NMR). A transient red coloration of the solution occurred during the addition of ZnR_2. The solvent was evaporated in vacuo at ambient temperature resulting in a white residue which was crystallized from hexane at −80 °C (yield >80%).

Syntheses of $[RZn(R^1)N=C(R^2)C(R^3,R)O]_2$ (2a–e). Compounds 2a,d. A diethyl ether solution (100 mL) of *t*-BuN=CHC(Me)=O (10 mmol) was added dropwise to a suspension of an equimolar amount of ZnR_2 (R = *p*-tolyl, Me) in diethyl ether (50 mL) at −100 °C. A transient red coloration of the reaction mixture was observed, and eventually a pale yellow colored solution was formed. The solvent was evaporated in vacuo at ambient temperature. Washing of the residue with cold hexane (3 × 20 mL) resulted in the formation of a white product that was recrystallized from CH_2Cl_2/hexane, 1:5 (80% isolated yield).

Compounds 2b,e. A diethyl ether solution (50 mL) of *t*-BuN=CHC(Me)=O (10 mmol) was added dropwise to a suspension of an equimolar amount of ZnR_2 (R = *tert*-butyl, benzyl) in diethyl ether (100 mL) at −100 °C. The resulting solution was intensively dark colored, which changed slowly to pale yellow at −20 °C. [The reaction was carried out as a titration: further addition of ZnR_2 was stopped when the last drop of the α-imino ketone (at −20 °C) did not cause a blue coloration.] The solvent was evaporated in vacuo at ambient temperature. The resulting residue was washed with cold hexane (3 × 20 mL) and then recrystallized from CH_2Cl_2/hexane, 1:5 (55% isolated yield).

Hydrolysis of the Organozinc Complexes. A detailed description of the synthesis of the α-amino ketones and α-hydroxy imines obtained from hydrolysis of **1** and **2** will be published in a future paper.[14] These experiments were carried out as an one-pot reaction; i.e., reaction of the α-imino ketones with ZnR_2 was followed by hydrolysis of the resulting organozinc compounds **1** and **2** with H_2O. The α-amino ketones and α-hydroxy imines were isolated in yields better than 90%.

Reaction of the α-Amino Ketones and α-Hydroxy Imines with ZnR_2. Reformation of the Organozinc Complexes 1a and 2b and Formation of 2c. The pure α-amino ketone Et(*t*-Bu)NCH_2C(Me)=O or α-hydroxy imine *t*-BuN=C(H)C(Me,*t*-Bu)OH (10 mmol) was dissolved in 50 mL of benzene. A hexane solution of equimolar amounts of either $ZnEt_2$ or Zn-*t*-Bu_2 was added. The reaction solution was stirred for 3 h at 60 °C after which time alkane evolution ceased. The solvent was evaporated in vacuo, and the resulting products **1a** and **2b** respectively were recrystallized from hexane (yield >70%).

New organozinc products, with substituents different from those of the parent compounds, were also synthesized. For example, the 1:1 molar reaction of $ZnEt_2$ and *t*-BuN=C(H)C(Me,*t*-Bu)OH in benzene at 60 °C afforded in 3 h dimeric $[EtZn(t\text{-Bu})N=C(H)C(Me,t\text{-Bu})O]_2$ (**2b**) in 75% yield.

Physical Measurements. ^1H NMR spectra were recorded on a Bruker WM-250, Varian T-60, or Varian A-60 NMR spectrometer and ^{13}C NMR spectra on a Bruker WP-80 or Varian CFT-20 NMR spectrometer. Off-resonance ^{13}C NMR spectra were recorded for all the compounds to enable assignment. Cryoscopic molecular weight determinations of various organozinc compounds **1** and **2** in benzene were carried out under dry, oxygen-free nitrogen in a homemade apparatus with an accuracy of ±10%. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO Zeist, The Netherlands.[13] The ^1H and ^{13}C NMR spectroscopic data are summarized in Tables IV and V.

X-ray Data Collection, Structure Determination, and Refinement of $[EtZn(Et)(t\text{-Bu})NC(H)=C(Me)O]_2$ (1a).

Table I. Crystal Data and Numerical Details of the Structure Determination of $[EtZn(Et)(t\text{-Bu})NC(H)=C(Me)O]_2$ (1a)

(a) Crystal Data

formula	$C_{22}H_{46}N_2O_2Zn_2$
mol wt	501.36
cryst system	triclinic
space group	$P\bar{1}$
a, Å	7.57 (1)
b, Å	8.82 (2)
c, Å	11.14 (1)
α, deg	102.6 (1)
β, deg	91.8 (1)
γ, deg	114.4 (2)
V, Å^3	655 (2)
Z	1
D_{calcd}, g cm^{-3}	1.271
F(000), electrons	268
μ(Mo Kα), cm^{-1}	19.0

(b) Data Collection

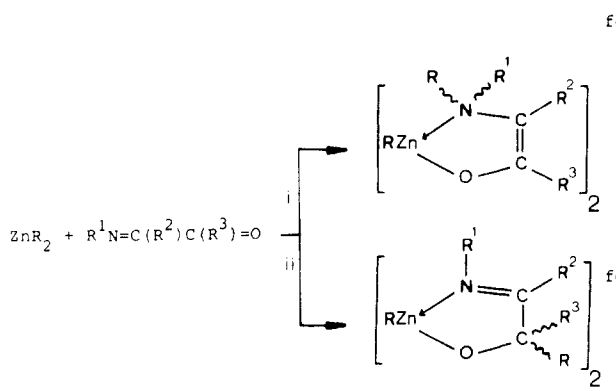
temp, K	295
radiatn, Å	0.710 69 (Zr filtered)
θ_{min}, θ_{max}	0.1, 20
ω, deg	$\Delta\omega = 1.6 + 0.35 \tan\theta$
cryst to detector, mm	173
hor and vert apert, mm	2, 6
max time/refl, s	90
refl refl	223
data set	*h*, −7→7; *k*, −8→8; *l*, −10→10
total reflctns	2442
total unique refl	1221
obsd data ($I > \sigma(I)$)	1051
total X-ray exp time, h	71
decay	4%

(c) Refinement

$R_F = \sum\|F_o - \|F_c\|\|/\sum\|F_o\|$	0.089
$wR_F = \{\sum w(F_o - \|F_c\|)^2/\sum wF_o^2\}^{1/2}$	0.085
w^{-1}	$(\sigma^2(F) + 0.0001F^2)/3.09$
no. of refined parameters	146
no. of reflctns	1051
$(\Delta/\sigma)_{max}$	0.4
min and max residual density, e Å^{-3}	−1.12 and 0.86
S	2.56

Crystals of $[EtZn(Et)(t\text{-Bu})NC(H)=C(Me)O]_2$ are colorless. Several specimens were sampled into Lindemann glass capillaries under nitrogen atmosphere. Subsequent examination with X-rays showed that all crystals were of limited quality as indicated by wide diffraction peaks and low resolution. The best crystal was used for data collection with an Enraf-Nonius CAD4F diffractometer. Crystal data and other numerical details of the structure determination are listed in Table I. Unit cell dimensions were calculated from the setting angles of 24 carefully centered reflections. A whole sphere of reflections up to $\theta = 20°$ was collected in the ω scan mode by using Zr-filtered Mo Kα radiation. The set of 2442 scanned reflections was averaged into a unique data set (R_{av} = 7.6%) and corrected for Lorentz, polarization, and decay effects. The structure was solved by standard Patterson and Fourier methods and refined on *F* by full-matrix least-squares techniques. Hydrogen atoms were introduced on calculated positions (C–H = 1.08 Å) and refined either in the riding mode on their carrier atoms or as rigid rotators (CH_3 groups) with one overall isotropic temperature factor (U = 0.113 (7) Å^2). Convergence was reached at R = 0.089. Table II lists the final positional parameter values of the non-hydrogen atoms. Scattering factors were those of Cromer and Mann, corrected for anomalous dispersion.[15] The structure determination and refinement were carried out on an in-house ECLIPSE S/230 minicomputer with

(13) See supplementary material paragraph at the end of this paper.
(14) van Vliet, M. R. P.; Van Koten, G.; Klaver, W. J.; Modder, J. F. *Recl. Trav. Chim. Pays-Bas*, in press.
(15) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321. (b) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.



for R=Et, R^1=t-Bu, R^2=H and R^3=Me (1a)
R=Et, R^1=$EtMe_2C$, R^2=H and R^3=Me (1b)
R=Et, R^1=benzyl, R^2=Me and R^3=Me (1c)
R=Et, R^1=t-Bu, R^2=H and R^3=Ph (1d)
R=n-Bu, R^1=t-Bu, R^2=H and R^3=Me (1e)
R=i-Bu, R^1=t-Bu, R^2=H and R^3=Me (1f)
R=i-Prop, R^1=t-Bu, R^2=H and R^3=Me (1g)
R=i-Prop, R^1=t-Bu, R^2=H and R^3=Ph (1h) (1)

for R=Me, R^1=t-Bu, R^2=H and R^3=Me (2a)
R=t-Bu, R^1=t-Bu, R^2=H and R^3=Me (2b)
R=p-tolyl, R^1=t-Bu, R^2=H and R^3=Me (2d)
R=benzyl, R^1=t-Bu, R^2=H and R^3=Me (2e)

Table II. Positional Parameters for the Non-Hydrogen Atoms and Their Estimated Standard Deviation for $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$ (1a)

atom	x/a	y/b	z/c
Zn(1)	−0.0099 (3)	0.0241 (3)	−0.1320 (2)
O(1)	−0.195 (2)	−0.029 (2)	−0.004 (1)
N(1)	−0.217 (2)	−0.237 (2)	−0.239 (1)
C(1)	−0.519 (3)	−0.222 (3)	0.027 (2)
C(2)	−0.354 (2)	−0.188 (2)	−0.054 (2)
C(3)	0.361 (3)	0.287 (3)	0.157 (2)
C(4)	−0.303 (3)	−0.226 (3)	−0.355 (2)
C(5)	−0.386 (3)	−0.090 (3)	−0.335 (2)
C(6)	−0.125 (3)	−0.357 (3)	−0.266 (2)
C(7)	0.055 (3)	−0.275 (3)	−0.330 (2)
C(8)	−0.061 (3)	−0.386 (3)	−0.145 (2)
C(9)	−0.250 (3)	−0.534 (2)	−0.349 (2)
C(10)	0.100 (3)	0.230 (2)	−0.201 (2)
C(11)	0.151 (3)	0.216 (3)	−0.327 (2)

a locally adapted implementation of the SHELX-76 package.[16] All derived geometry calculations were done with the programs of the EUCLID package on the CYBER-855 of the University of Utrecht.[17]

Results

The reactions of ZnR_2 with α-imino ketones follow a distinct reaction course (see eq 1) in which product formation is almost quantitative. For this reason isolation and characterization of the pure organozinc products was possible. The nature of the R groups bonded to zinc, i.e., methyl, primary, secondary, or tertiary alkyl, aryl, or benzyl, appeared to be the main factor involved in determining the type of organozinc species formed.

In the case of *primary* (except methyl) and *secondary* alkyl groups, transfer of the organo group from Zn to the imino nitrogen atom of the α-imino ketone was observed leading to the formation of a new organozinc species (**1**) with a $[R(R^1)NC(R^2)=C(R^3)O]^-$ bidentate coordinated β-amino enolate monoanion. However, $ZnMe_2$ and di-*tert*-alkyl- and diarylzinc compounds afforded with the same α-imino ketone substrates organozinc compounds of type **2** containing the $[R^1N=C(R^2)C(R^3,R)O]^-$ monoanionic α-iminoalkanolate. These compounds, **2**, originate from a transfer of the organo group from Zn to the carbonyl carbon atom.

The organozinc compounds **1** and **2** were isolated in yields greater than 90%. Both **1** and **2** are soluble in hexane, dichloromethane, and aromatic solvents and are extremely sensitive toward H_2O and O_2. Elemental analytical data confirmed the stoichiometries shown for the products in eq 1.[13] Cryoscopic molecular weight determinations revealed that the organozinc compounds **1** and **2** are dimeric in benzene.[13] Although association degrees up to eight have been found for other organozinc complexes, the presence of bulky organo groups at the coordinating donor atoms may favor the formation of monomeric species even when this would imply three-coordination at the zinc atom. The latter aspect is illustrated by the structure of monomeric $RZn(R)(R^1)NC(H)=C(H)NR^1$, in which the alcoholate O atom present in **1** is replaced by an amino NR group.[5]

Table III. Relevant Geometrical Data for $Zn_2C_{22}H_{46}N_2O_2$ (1a)[a]

Bond Distances (Å)

Zn(1)-Zn(1′)	3.069 (3)	O(1)-C(2)	1.40 (2)
Zn(1)-O(1)	2.02 (1)	C(1)-C(2)	1.54 (3)
Zn(1)-O(1′)	2.12 (1)	C(2)-C(3)	1.27 (3)
Zn(1)-N(1)	2.21 (2)	C(4)-C(5)	1.55 (4)
Zn(1)-C(10)	1.99 (2)	C(6)-C(7)	1.54 (3)
N(1)-C(3)	1.43 (2)	C(6)-C(8)	1.53 (3)
N(1)-C(4)	1.47 (3)	C(6)-C(9)	1.51 (3)
N(1)-C(6)	1.47 (3)	C(10)-C(11)	1.46 (3)

Bond Angles (deg)

O(1)-Zn(1)-O(1′)	84.2 (5)	Zn(1′)-O(1)-C(2)	116 (1)
O(1)-Zn(1)-N(1)	82.8 (5)	O(1)-C(2)-C(1)	112 (2)
O(1)-Zn(1)-C(10)	130.5 (7)	O(1)-C(2)-C(3)	123 (2)
O(1′)-Zn(1)-N(1)	114.3 (6)	C(1)-C(2)-C(3)	125 (2)
O(1′)-Zn(1)-C(10)	112.0 (7)	N(1)-C(3)-C(2)	123 (2)
C(10)-Zn(1)-N(1)	124.9 (7)	N(1)-C(4)-C(5)	113 (2)
Zn(1)-N(1)-C(3)	102 (1)	N(1)-C(6)-C(7)	108 (2)
Zn(1)-N(1)-C(4)	109 (1)	N(1)-C(6)-C(8)	109 (2)
Zn(1)-N(1)-C(6)	113 (1)	N(1)-C(6)-C(9)	117 (2)
C(3)-N(1)-C(4)	111 (1)	C(7)-C(6)-C(8)	110 (2)
C(3)-N(1)-C(6)	112 (2)	C(7)-C(6)-C(9)	107 (2)
C(4)-N(1)-C(6)	110 (2)	C(8)-C(6)-C(9)	106 (2)
Zn(1)-O(1)-Zn(1′)	95.8 (5)	Zn(1)-C(10)-C(11)	122 (2)
Zn(1)-O(1)-C(2)	109 (1)		

Torsion Angles (deg)

O(1)-C(2)-C(3)-N(1)	−7 (3)	C(5)-C(4)-N(1)-C(6)	−174 (2)
C(4)-N(1)-C(6)-C(8)	−172 (2)	C(3)-N(1)-C(6)-C(8)	−49 (2)

Least-Squares Plane[b] and Deviations (Å)

$-5.62\ (4)x + 6.91\ (4)y - 5.72\ (7)z - 0.957\ (8) = 0$

Zn(1)*	0.02 (1)	C(3)*	−0.01 (3)
O(1)*	−0.04 (2)	C(1)	0.27 (3)
N(1)*	−0.01 (3)	Zn(1′)	−0.194 (1)
C(2)*	0.04 (3)	O(1′)	−1.88 (2)

[a] Esd's in the last digit are in parentheses. The prime indicates the symmetry operation −x, −y, −z. [b] Least-squares plane equations in terms of fractional coordinates. Atoms that determine the plane are indicated with an asterisk.

Dinuclear N-Alkylated Product 1. Unambiguous proof for a dimeric structure of the organozinc β-amino vinyl alcoholates **1** in the solid state comes from the X-ray

(16) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England.
(17) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford; 1982; p 528.

Table IV. The ^1H and ^{13}C NMR Data[a] of $[RZn(R)(R^1)NC(R^2)=C(R^3)O]_2$ (1a-h)

compd	R to Zn	R to N	R_1	R_2	R_3
			^1H NMR		
1a	Et, 0.53 m;[b] 1.60 t	1.08 t; 2.06/2.79 m[b]	*t*-Bu, 1.14 s	H, 4.16 s	Me, 1.93 s
1b	Et, 0.55 m;[b] 1.61 t	1.10 t; 2.10/2.79 m[b]	$EtMe_2C$, 0.78 t; 0.98/1.16 s;[b] 1.62 q	H, 4.18 s	Me, 1.94 s
1c	Et, 0.50 m;[b] 1.60 t	1.06 t; 2.05/2.65 m[b]	benzyl, 4.00 m;[b] 7.30 m	Me, 1.50 s	Me, 2.00 s
1d	Et, 0.23 m;[b] 1.26 t	1.00 t; 2.08/2.79 m[b]	*t*-Bu, 1.24 s	H, 4.96 s	Ph, 7.50 m
1e	*n*-Bu, 0.53 m; 1.23 t; 1.50–1.80 m	0.86 t; 1.50–1.80 m; 2.19 m; 2.86 m	*t*-Bu, 1.18 s	H, 4.29 s	Me, 1.95 s
1f	*i*-Bu, 0.5–2.3 m	0.5–2.3 m	*t*-Bu, 1.19 s	H, 4.21 s	Me, 1.90 s
1g	*i*-Pr, 0.71 m; 0.90 d/d[b]	1.10 d/d;[b] 3.45 m	*t*-Bu, 1.22	H, 4.30 s	Me, 1.90 s
1h	*i*-Pr, 0.68 m; 0.85 d/d[b]	1.08 d/d;[b] 3.24 m	*t*-Bu, 1.20 s	H, 4.88 s	Ph, 7.45 m
			^{13}C NMR		
				N–C CO	
1a	1.8; 12.4	13.3; 45.0	26.5; 58.6	104.6 160.0	20.8
1b	1.9; 12.4	13.3; 44.0	9.6; 21.7/23.0;[b] 31.5; 58.5	104.4 160.0	20.8
1c	–0.4; 12.0	13.3; 46.4	59.6; 128; 128.3; 131.3; 135.6	110.8 153.8	19.6; R^2, 8.1
1d	2.2; 12.4	13.3; 45.5	26.6; 59.2	105.0 160.3	127.6; 130.6; 133.5; 139.7
1e	10.7; 21.0; 26.5; 30.5	14.3; 29.8; 32.1; 51.5	26.7; 58.7	105.5 158.6	21.6
1f			26.4; 59.5	104.9 163.5	20.7
1g	5.4; 16.8	16.0/19.4;[b] 51.3	26.1; 59.4	106.3 159.7	20.2

[a] In C_6D_6. All values are in parts per million relative to external Me_4Si: s = singlet, d = doublet, t = triplet, m = multiplet. Multiplicity (for ^{13}C NMR), obtained from off-resonance spectra, is in agreement with the proposed assignments. [b] Diastereotopic groups or (geminal)-hydrogen atoms.

structure determination of compound **1a**, $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$.

The crystal structure of **1a** is triclinic. The unit cell contains one discrete dimer, located on a crystallographic inversion center. Figure 1 presents an overview of the molecule along with the adopted numbering scheme. (An ORTEP view has been deposited). Bond distances and angles are given in Table III.

The molecule contains a central, four-membered Zn_2O_2 ring that links the two halves of the dimer around a center of symmetry. Coordination of the amino nitrogen atom to zinc results in the formation of a five-membered ZnOCCN chelate ring and completes four-coordination at the zinc atom. The C(2)—C(3) bond length of 1.27 (3) Å is as expected for a C=C double bond and establishes the conversion of the neutral α-imino ketone ligand into a monoanionic β-aminovinyl alcoholate group.

The central Zn_2O_2 ring is flat. Both five-membered rings, one above the Zn_2O_2 plane and the second under the plane with an angle between the five- and four-membered rings of 116 (1)°, are mutually parallel oriented. The five-membered chelate ring is essentially planar as may be seen from the maximum deviations of 0.04 (2) Å of the ring atoms from the corresponding least-squares plane (Table III).

The Zn and O atoms are four- and three-coordinate, respectively, but in terms of bonding geometry may formally be considered to be sp^3-hybridized. The Zn(1′)–O(1)–C(2) angle of 116 (1)° is considerably larger than the tetrahedral value, which no doubt results from the Zn(1)–O(1)–Zn(1′) angle of 95.8 (5)°. The Zn(1)–O(1)–Zn(1′) and the O(1)–Zn(1)–O(1′) angles of 95.8 (5)° and 84.2 (5)°, respectively, are in good agreement with the corresponding angles of 95.9 (6)° and 83.8 (6)° found in tetrameric $[MeZnOMe]_4$.[18] The Zn–O bond lengths in the Zn_2O_2 ring of 2.02 (1) and 2.12 (1) Å are not significantly different from these bond lengths (2.00 and 2.09 Å) found in the

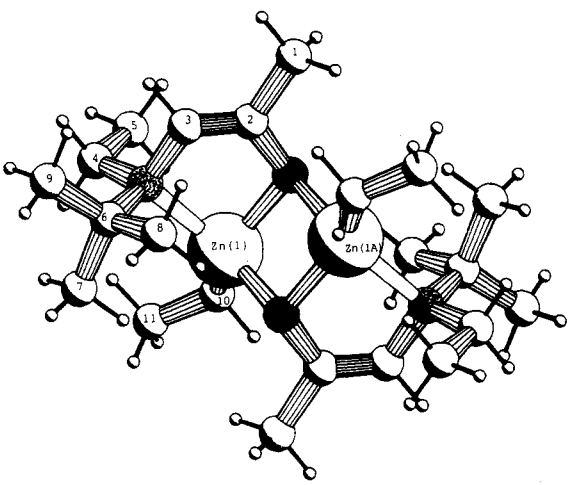


Figure 1. PLUTO drawing of $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$ (**1a**). The adopted numbering scheme is indicated.

Zn_2O_2 rings of bis{phenyl(acetylacetonato)zinc(II)}bis(acetylacetonato)zinc(II).[19] The Zn atoms in **1a** have bond angles of 84.2 (5)° due to ring strain so that the atomic orbitals used in forming the bonds to O will have increased p character and consequently the orbitals for bonding to the ethyl C atom have greater s character than their formal hybridization states suggest. The Zn–C distance of 1.99 (2) Å is in good agreement with the 1.963 (5) Å Zn–C bond length found in $Et_2Zn_4[N(Ph)CO_2Me]_6$.[20] About the N(1) atom only one angle, i.e., Zn(1)–N(1)–C(3) = 102(1)°, is considerably smaller than the tetrahedral value, which probably is connected with the ring strain in the five-membered chelate ring. The Zn–N dative bond length of 2.21 (2) Å is significantly larger than the value of 2.07 (1) Å observed in bis{methyl(diphenylamino)zinc} in which the N atom is covalently bonded to and bridging between the

(18) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2046.

(19) Spek, A. L. *Cryst. Struct. Commun.* **1973**, *3*, 535.

(20) van Santvoort, F. A. J. J.; Krabbendam, H.; Spek, A. L.; Boersma, J. *Inorg. Chem.* **1978**, *17*, 388.

Table V. The ^1H and ^{13}C NMR Data of [RZn(*t*-Bu)N=CHC(Me,R)O]$_2$ (2a–e)

compd	R to Zn	R to C	*t*-Bu	H	Me
		^1H NMR			
2a	Me, −0.43 s	1.36 s	1.13 s	7.53 s	1.36 s
2b	*t*-Bu, 0.97 s	1.47 s	1.03 s	7.89 s	1.17 s
2c	Et, 0.36 m;[b] 1.59 t	*t*-Bu, 1.04 s	1.12 s	7.81 s	1.47 s
2d	*p*-tolyl, 2.10 s; 7.14 m	2.23 s; 7.20 m	1.08 s	7.63 s	1.39 s
2e	benzyl, 1.90 m;[b] 7.3 m	2.61 m;[b] 7.60 m	1.16 s	7.85 s	1.24 s
		^{13}C NMR			
				N=*C* CO	
2a	Me, −9.9	29.6	29.7; 57.1	175.0 74.5	29.6
2b	*t*-Bu, 9.8; 21.0	25.2; 37.3	29.6; 57.7	178.2 75.7	28.1
2e	benzyl, 23.5; 120.6, 126.8, 128.0, 131.1	49.5; 126.5, 128.2, 138.0, 151.1	29.9; 57.4	176.6 77.1	26.1

[a] In C_6D_6. All values are in parts per million relative to external Me_4Si: s = singlet, t = triplet, m = multiplet. Multiplicity (for ^{13}C), obtained from off-resonance spectra, is in agreement with the proposed assignments. [b] Diastereotopic CH_2 protons. [c] R to C is *t*-Bu.

zinc atoms.[21] This Zn–N bond is, however, similar to the distance of 2.19 (1) Å for the dative Zn–N bond found in dimeric [HZnN(Me)CH_2CH_2NMe$_2$]$_2$.[22]

The ^1H NMR spectra of the organozinc compounds **1a–1h** (see Table IV) are in agreement with structures consisting of an alkylzinc entity to which a *cis*-[R(R^1)NC(R^2)=C(R^3)O]$^-$ monoanion is bidentate bonded. The imino hydrogen resonances (R^2 = H; **1a**, **1b**, **1d–h**) are shifted from the low-field region of the α-imino ketones (ca. 7.5 ppm) to the region characteristic for vinylic hydrogen atoms (ca. 4.5 ppm). The ^{13}C NMR spectra (Table IV) show two different olefinic carbon atom resonances at ca. 105 (*NC*) and ca. 160 ppm (*CO*). The amino N atom in these organozinc compounds (**1a–h**), containing the transferred alkyl group, is a stable chiral center since its coordination to zinc prevents the occurrence of pyrimidal inversion. The chirality of the tetrahedral amino N center is reflected, for example, by the NMR resonance patterns observed for **1b** (see Table IV). The methyl groups in the prochiral EtMe$_2$C nitrogen substituent of [EtZn(Et)(EtMe$_2$C)NC(H)=C(Me)O]$_2$ (**1b**) are diastereotopic as can be seen in both the complex ^1H and ^{13}C NMR patterns. Also the prochiral CH_2 and *i*-Pr groupings in compounds **1a–h** are diastereotopic (see Table IV).

The fact that for the compounds containing chiral amino N centers only one pattern is observed indicates that the dimeric species are actually present as the enantiomeric pair of one diastereomer (i.e., either *RR*/*SS* or *RS*/*SR*). The X-ray structure of **1a** (see Figure 1) showed that this dinuclear compound is present in the solid as the *RS*/*SR* enantiomeric pair. Also shown by Figure 1 is a possible reason for this combination of configurations at both amino N centers because it is only in this dimeric structure of the enantiomers that the Et(Zn) and the Et(N) groups (instead of the more bulky *t*-Bu group) are on the same side of the chelate ring. In the alternative structure, having the opposite configuration at one of the amino N centers, the Et(Zn) and the bulkier *t*-Bu(N) group would be on the same side.

Dinuclear, Carbonyl C-Atom-Alkylated or -Arylated Products 2. The NMR spectra of the zinc compounds **2a–e** showed the formation of carbonyl C-addition products. The ^1H NMR spectra (Table V, **2a–e**) are in agreement with structures consisting of an alkylzinc entity

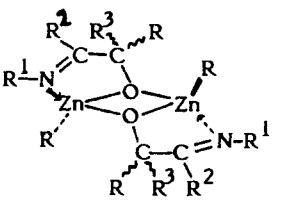


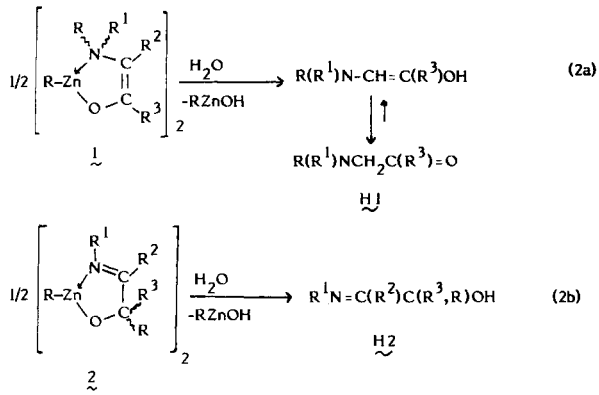
Figure 2. Proposed structure of the dimeric carbonyl C-addition products [RZn(R^1)N=C(R^2)C(R^3,R)O]$_2$ (**2**).

that is chelate-bonded to an (*E*)-imine, [R^{1}N=C(R^2)C(R^3,R)O]$^-$, monoanion. Each of the organozinc compounds contains a four-coordinate zinc atom, see Figure 2. In compounds **2b–e** the carbonyl C atoms are the chiral centers that chirality is reflected, for example, by the ^1H NMR spectrum of **2c** (Table V). The *CH*$_2$ hydrogen atoms of the ethylzinc group are diastereotopic that result in spectra with complex multiplet resonances patterns (ABX$_3$) for these protons. The ^{13}C NMR spectra of **2a**, **2b**, and **2e** (see Table V) showed two resonances for the carbon atoms of the NCCO skeleton: one resonance at ca. 177 ppm, which is a typical value for the ^{13}C resonance of an N-coordinated N=C grouping, and a second resonance at ca. 75 ppm, which is in the expected region of the resonances of alkoxy carbon nuclei in a C(R^3,R)O unit. According to the ^1H NMR spectrum the reaction mixture of *t*-BuN=CHC(Me)=O with ZnBz$_2$ consisted of both the N- and the carbonyl C-addition products in an 1:4 molar ratio. Up to now we succeeded only in the isolation of the pure carbonyl addition compound [BzZn(*t*-Bu)N=CHC(Me,Bz)O]$_2$ (**2e**) from this mixture by crystallization (Table V). Also in this compound the AB pattern of the benzylic protons confirmed the presence of a chiral C center in the addition product. In analogy with the above-mentioned organozinc derivatives **1** the compounds **2** show only a single NMR resonance pattern. This strongly suggests that similar to the selective formation of the dinuclear structure of **1** dimeric **2** also exists in only one enantiomeric pair of diastereomers.

Reformation of 1 and 2 from the α-Amino Ketones and α-Hydroxy Imines. Further structural confirmation for the presence of the N,O monoanionic bidentate ligands in the organozinc compounds **1** and **2** comes from hydrolysis experiments. Hydrolysis of **1** and **2** afforded in quantitative yields new α-amino ketones H1 and α-hydroxy imines H2, respectively, according to eq 2.

The organic aspects of these reactions and the formation of the new organic products by hydrolysis of the organozinc intermediates will the subject of a future paper; see ref 14.

(21) Bell, N. A.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect C: Cryst. Struct. Commun.* **1983**, *C39*, 1182.
(22) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2950.

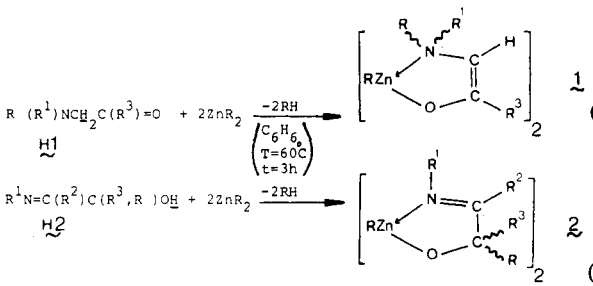


(2a)

(2b)

In general, reactions between ZnR_2 and a ligand containing an active hydrogen in a 1:1 molar ratio may result in the formation of the metal-containing product and the corresponding hydrocarbon. It is very interesting to find that in this way also the organozinc compounds **1** and **2** can be reformed almost quantitatively. In particular the reformation of the complexes **1**, $[RZn(R)(R^1)NC(H)=C(Me)O]_2$, which have the *Z* configuration at the vinylic group, is of importance. The formation of the α-amino ketone by hydrolysis of the zinc complexes **1** (see eq 2) is the result of a subsequent tautomerization of the initially formed β-aminovinyl alcohol into the α-hydroxy imines. The reverse reaction of the latter α-hydroxy imines with ZnR_2 compounds is very clean and seems therefore a nice method to generate a stable (*Z*)-β-aminovinyl alcoholate entity.

The zinc complexes, obtained in this way (see eq 3), and samples of authentic complexes obtained via eq 1 showed identical spectra. The route of eq 3 could also be used for the preparation of organozinc derivatives that otherwise via the direct reaction could only be obtained as a mixture of the C- and N-alkylated products. An example is the clean formation of the pure C-alkylated product **2e** via the 1:1 molar reaction of *t*-BuN=CHC(Me,Bz)OH with $ZnBz_2$; see eq 3b.



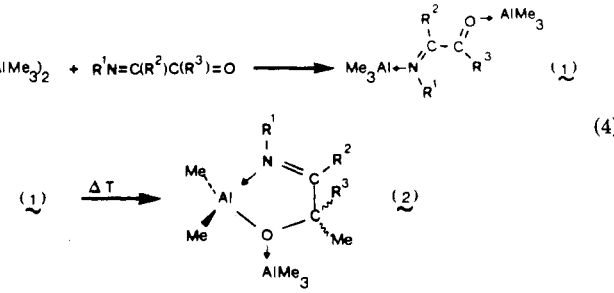
(3a)

(3b)

Discussion

Formation of the Donor–Acceptor Complexes. In the first stages of the reaction of ZnR_2 with α-imino ketones the corresponding donor–acceptor (1:1 coordination) complexes are formed. The nature of the binding, i.e., monodentate N- or O-coordination or N,O-chelate coordination, could not be studied directly by NMR because of low solubility of the complexes as well as of the extreme reactivity toward further reaction.

In a separate study we showed that the α-imino ketone ligands, which exist as free ligands in the nonplanar gauche conformation,[7,9] coordinate via the imine nitrogen atom to the *trans*-$PtCl_2(PR_3)$ moiety.[23] More importantly, it could also be established by an X-ray structure determination that in $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(MeN{=}C(Ph)C(Ph){=}O)\}]$ the N=CC=O skeleton of the α-imino ketone has the nonplanar gauche conformation and is coordinated via both the carbonyl O and the imine N atom in the bridging coordination mode.[24] The relevance of the aluminum complex for the understanding of the complex formation in the present $ZnR_2/R^1N{=}C(R^2)C(R^3){=}O$ system is indicated by its subsequent conversion at higher temperatures into the carbonyl C-alkylated product (see eq 4).[25]



(4)

So far, stable organozinc complexes with a chelate-bonded α-imino ketone could not be isolated. However, the characteristic dependence of the color of the complexes of the organo group R bound to Zn, i.e., orange for R = Me to purple for R = *t*-Bu, had also been observed for the ZnR_2-2,2′-bipyridine and $ZnR_2(R^1\text{-DAB})$ complexes (see A in Scheme I) whose ligands likewise contain a 1,4-dihetero-conjugated π system.[4b,5,26] In the case of A the σ,σ'-N,N′-chelate bonding mode could be studied in detail by ^1H and ^{13}C NMR data at low temperature. The same trend is found for the deepening of the color of both the ZnR_2/R^1-DAB and the ZnR_2/α-imino ketone complexes with increasing Hammett σ value of the group R bound to zinc.[26b] This color change points to occurrence of charge transfer within these complexes (see also A in Scheme II) from the filled, zinc–carbon bonds into the LUMO of the ligand. This LUMO has bonding character between the central carbon atoms of the NCCX skeleton but is antibonding in nature between carbon and the heteroatom (C–O and C–N, respectively).

Complete one-electron transfer from the organozinc entity to the chelate-bonded ligand then generates the radical pair B during which process the coordination geometry of Zn changes from tetrahedral in A to trigonal planar in B. As has been pointed out by Kaim and by us, in the tetrahedral situation the σ-Zn–C bonds are well-positioned for interaction with the π^* orbital of the acceptor.[27] In fact as the homolytic cleavage of one of the σ-Zn–C bonds turns on, the other Zn–C bond moves into the plane of the ZnN=C—C=O chelate that generates a situation (before B) with the R• radical close to and above the organozinc radical complex. It is clearly the chelate bonding mode as well as the π-acceptor property of the 1,4-dihetero conjugate π system that lower the barrier to this inner-sphere electron-transfer process and are the driving forces for the homolytic Zn–C bond cleavage.

The further events, which determine the type of product formed, then depend on the nature of the organo radical

(23) van Vliet, M. R. P.; van Koten, G.; van Beek, J. A. M.; Vrieze, K.; Muller, F.; Stam, C. H. *Inorg. Chim. Acta* **1986**, *112*, 77.

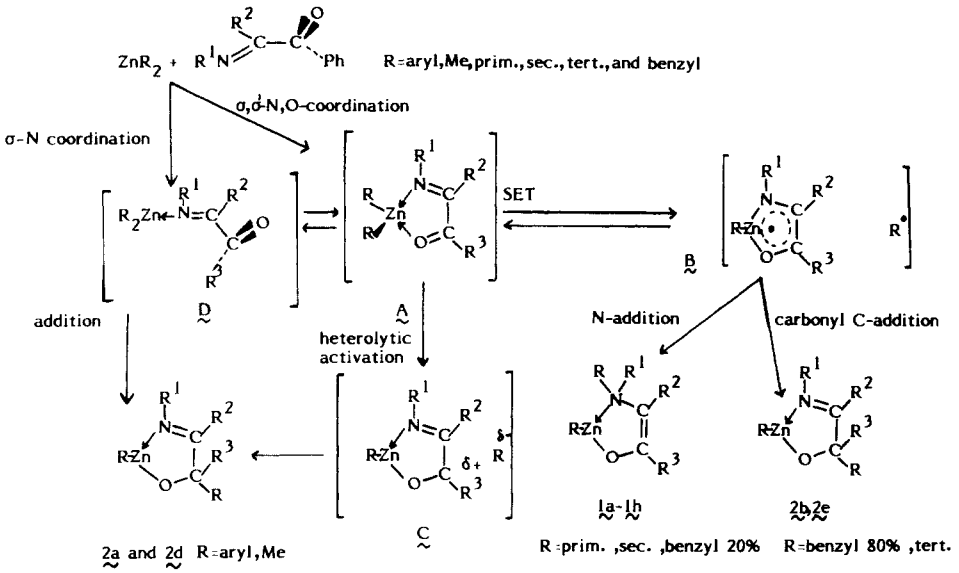
(24) van Vliet, M. R. P.; van Koten, G.; Rotteveel, M. A.; Schrap, M.; Vrieze, K.; Kojić-Prodić, B.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1986**, *5*, 1389.

(25) van Vliet, M. R. P.; van Koten, G.; de Keijser, M. S.; Buysingh, P.; Vrieze, K., accepted for publication in *Organometallics*.

(26) (a) Thiele, K. H.; Schroder, S. *Z. Anorg. Allg. Chem.* **1965**, *337*, 14. (b) Noltes, J. G.; van den Hurk, J. W. G. *J. Organomet. Chem.* **1965**, *3*, 222. (c) Coates, J. E.; Green, S. T. E. *J. Chem. Soc.* **1962**, 334. (d) Thiele, K. H.; Rau, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 127.

(27) (a) Louwen, J. N.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1984**, 2683. (b) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160.

Scheme II. Proposed Mechanism Explaining All Products Formed in the Reactions of ZnR_2 with α-Imino Ketones[a]



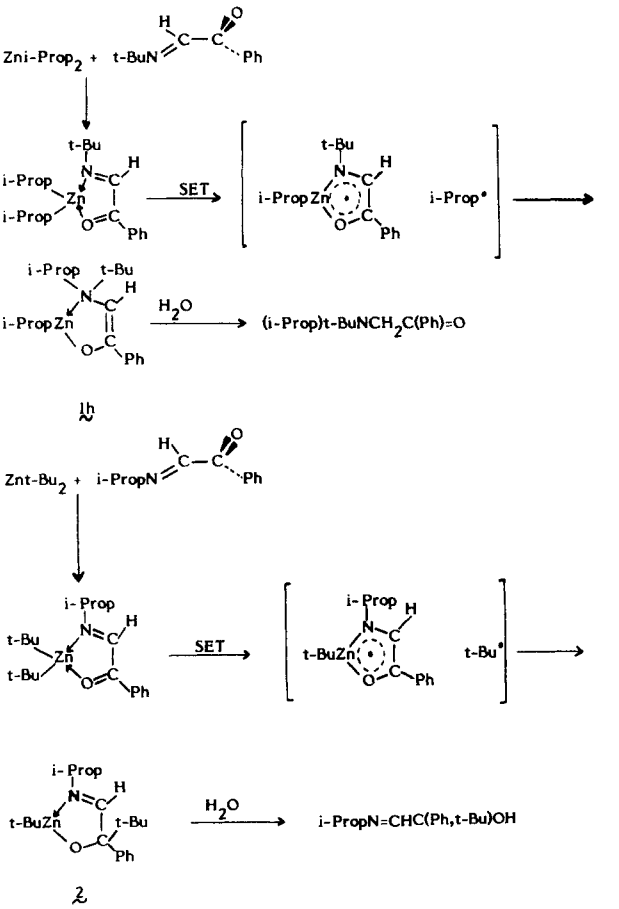
[a] The mechanism includes, starting from the chelate coordination mode A, both homolytic B and heterolytic C activation. Starting from monodentate N-coordination D, a direct addition is proposed.

and the distribution of the spin density on the various atoms in the chelate ring of the organozinc radical. The latter aspect could be studied for [RZn(R^1-DAB)]• (vide infra)[4b,5,28] and [RZn(R^1-Pyca)]• (R^1-Pyca is R^1N=CH-2-py), but [RZn(α-imino ketone)]• is clearly too reactive to be studied in detail by ESR.

Product Formation. Whereas reactions of dialkylzinc compounds with primary and secondary alkyl groups with (*N-tert*-butylimino)propanone (*t*-BuN=CHC(Me)=O) give rise to the formation of N-alkylated products **1**, di-*p*-tolyl-, dimethyl-, and di-*tert*-butylzinc afford exclusively the carbonyl C atom addition products **2**; see Scheme II. Dibenzylzinc give rise to formation of a mixture of N- and carbonyl C-addition products. If we focus our attention on the product formation in the alkyl series, R = methyl, ethyl, isopropyl, and *tert*-butyl, we observe two breaking points: one between methyl and ethyl (C- vs. N-alkylation) and a second between isopropyl and *tert*-butyl (N- vs. C-alkylation). These two striking alterations indicate a change in mechanism of the reaction.

On the basis of the fact that product formation for R = Et, *i*-Pr, and *t*-Bu strongly resembles the product formation in the ZnR_2/R^1-DAB system, we propose that for these R groups a similar mechanism is operative in the ZnR_2/α-imino ketone system. Initial N,O-chelate complexation (see complexes A in Scheme II) is followed by SET leading to the formation of radical pair B. Subsequently, the organo radical is trapped at either the N center (N-alkylation) or at the carbonyl C center (carbonyl C-alkylation) (see Scheme II). It must be noted that the ultimate site of addition may be preceded by attack under kinetic control of a different site and that for steric reasons alkyl shift occurs that then generates the thermodynamically more stable product. This has also been found for $Et_2Al(t\text{-Bu})NC(H)=C(H)N(t\text{-Bu,Et})$ which on heating rearranges to $Et_2Al(t\text{-Bu})N=CH-CH(t\text{-Bu})NEt$ with the *t*-Bu group bonded to the carbon atom.[4b] Subsequent alkyl shifts may also account for the fact that in the reactions of ZnR_2 with α-imino ketones products originating from attack at the imine C center are not found that may be surprising because in the case of the ZnR_2/R^1-DAB system also imine C-alkylation is observed.

Scheme III. Comparison of the Reactions of Zn-*i*-Pr_2 and Zn-*t*-Bu_2 with *t*-BuN=CHC(Ph)=O and *i*-PrN=CHC(Ph)=O, Respectively, in Order To Investigate the Influence of Sterical Interference on the Ultimate Position of Addition



In order to investigate in more detail the influence of steric interference on the product formation, we compared

(28) Jastrzebski, J. T. B. H.; Klerks, J. M.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *210*, C49.

the Zn-*t*-Bu_2/*i*-PrN=CHC(Ph)=O and the Zn-*i*-Pr_2/*t*-BuN=CHC(Ph)=O systems. Reaction of Zn-*i*-Pr_2 with *t*-BuN=CHC(Ph)=O gave a N-alkylated product (compound **1h**, Table IV), indicating that the compound with the *i*-Pr and *t*-Bu groups at the same N center is stable. Interestingly, Zn-*t*-Bu_2 reacted with *i*-PrN=CHC(Ph)=O to give a carbonyl C-alkylated product (see Scheme III). If only the steric interference between the R^1 substituent and the migrating R group would be responsible for the difference between the reactivity pattern of Zn-*i*-Pr_2 and Zn-*t*-Bu_2 with the α-imino ketones, the formation of the same reaction products would be expected because the steric interference of R and R^1, i.e., *t*-Bu/*i*-Pr• and *i*-Pr/*t*-Bu•, is equal. Furthermore, reaction of Zn-*t*-Bu_2 with MeN=C(Ph)C(Ph)=O also afforded a carbonyl C-alkylated product that supports the view that steric effects alone cannot explain the nature of the products formed.

Product formation in the ZnR_2/α-imino ketone reactions for R = Et, *i*-Pr, benzyl, and *t*-Bu, can be rationalized, however, when the different alkyl radical activity and nucleophilicity of the radicals are taken into account. An order of radical reactivity can be defined by the strength of the C–H bond in the radical center, i.e., aryl• > Me• > *i*-Pr• > *t*-Bu• > Bz•.[29,30] The reactivity pattern of the intermediate radical pair B (see Scheme II) then reflects the relative stability of the R• radical. The cage effect of the solvent will cause R• and organozinc radical to undergo several collisions before they diffuse into the bulk of the solution. The more persistent C-centered radicals Bz• and *t*-Bu• are relatively less reactive than the primary and secondary alkyl radicals.[30] Moreover, the nucleophilicity of the alkyl radicals increases in the same order as their reactivity decreases, making the radicals more sensitive to polar influences in the ligand. This combination of radical reactivity and sensitivity to polar influences directs the attack of the *t*-Bu• to the more electrophilic carbonyl C center. For the slightly more reactive benzyl radical a less extreme situation is met that is reflected by the formation of a 20% yield of N-benzylated product. The most reactive primary alkyl radicals (except Me) will be trapped exclusively on the center with the highest spin density, which in the alkylzinc α-imino ketone radical is most probably the imino N center. In the case of the RZn-(R^1-DAB) radical this could be established by ESR measurements: the HOMO (SOMO) of this organozinc radical has antibonding character between N and C but is bonding between the central imine C atoms with a spin density distribution of 30% and 25% on the nitrogen and central C atoms, respectively.

A striking difference between the ZnR_2/R^1-DAB and the ZnR_2/α-imino ketone system is the fact that in the $ZnMe_2$/*t*-BuDAB reaction neither N- nor C-methylation is observed. Instead, exclusive formation of the MeZn(*t*-BuDAB) radical is obtained. This is in line with the fact that the Me radical, which is the most reactive one, is captured by the solvent before it can be trapped by the organozinc radical. A further difference of the two systems is the fact that whereas the diarylzinc/R^1-DAB complexes (see Scheme I) are stable, at least up to 140 °C, the diarylzinc/α-imino ketone complexes undergo rapid and exclusive carbonyl C-arylation.

These latter differences can be explained by assuming that in addition to the single electron-transfer route discussed above, for the diaryl- and dimethylzinc reaction another kinetic route is more favorable. This may comprise either a different coordination of the $ZnAr_2$ and $ZnMe_2$ to the α-imino ketone or occurrence of heterolytic activation instead of SET within the chelate complex A (see Scheme II).

A different coordination mode of the α-imino ketone in the dimethyl- and diarylzinc/α-imino ketone complexes from which subsequent product formation occurs seems a likely possibility. In the 1:1 complex D the α-imino ketone is not chelate bonded as in A but monodentate N coordinated. It has been demonstrated that diorganozinc compounds are Lewis acids which prefer N- to O-coordination as a result of the relatively soft character of the zinc center.[31] Actually N-coordination is also the preferred site of attack for other metal centers as we have observed in *trans*-[$PtCl_2(PEt_3)$\{σ-N-(*t*-BuN=CHC(Me)=O)\}].[23] It must be noted that the formation of the O-monodentate coordination product, as a first step of a direct 1,2 addition process, can be excluded because of the unreactivity of ketones in such reactions.[8]

The two coordination modes D and A are very closely related and most probably are in equilibrium with each other.[32] In D the α-imino ketone will have the nonplanar gauche conformation as has been established for analogous compounds.[7,9,23,24,32] This nonplanar gauche conformation is separated from the chelate bonding mode in A by only a rotation of 90° around the central C–C bond in the ligand and a concomitant change of the configuration at the Zn center from trigonal to tetrahedral.[27] It is the nature of the R groups at zinc that, for a given α-imino ketone, will have a large influence on which coordination prevales. In species of type D direct attack of the organo group R on the electrophilic carbonyl C center can occur.

The possibility that direct heterolytic activation within the chelate complex A occurs cannot be excluded. Methyl- and arylzinc compounds are known to give rise to relatively slow SET reactions as compared with the other dialkylmetal compounds whereas they react fast in polar addition reactions.[33] In the case of heterolytic activation (transition state C, Scheme II) we expect both methyl and *p*-tolyl carbanions to react as nucleophilic species with attack at the most electrophilic position in the NCCO skeleton, i.e., at the carbonyl C atom. Further studies are underway to clarify these points.

Acknowledgment. The X-ray data were kindly collected by Dr. A. J. M. Duisenberg. Prof. K. Vrieze is gratefully thanked for discussions. Investigations were supported in part (to A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. **1a**, 106189-24-6; **1b**, 106114-53-8; **1c**, 106138-90-3; **1d**, 106114-54-9; **1e**, 106114-55-0; **1f**, 106114-56-1; **1g**, 106114-57-2; **1h**, 106138-91-4; **2a**, 106114-58-3; **2b**, 106114-59-4; **2d**, 106114-60-7; **2e**, 106114-61-8; $ZnEt_2$, 557-20-0; An-*n*-Bu_2, 1119-90-0; Zn-*i*-Bu_2, 1854-19-9; Zn-*i*-$Prop_2$, 625-81-0; $ZnMe_2$, 544-97-8; Zn-*t*-Bu_2, 16636-96-7; ZnR_2 (R = *p*-tolyl), 15106-88-4; ZnR_2 (R = benzyl), 7029-30-3; *t*-BuN=CHC(Me)=O, 67122-50-3; $EtMe_2CN$=CHC(Me)=O, 67122-51-4; RN=C(Me)C(Me)=O (R = benzyl), 67122-52-5; *t*-BuN=CHC(Ph)=O, 91850-96-3; Et(*t*-Bu)NCH_2C-

(29) Ashby, A. C.; Goel, A. B. *J. Am. Chem. Soc.* **1981**, *103* 4983.
(30) (a) Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13. (b) Nonhebel, D. C.; Tedder, J. M.; Walton, J. C. *Radicals*; Cambridge University Press: New York, 1979.
(31) (a) Hofstee, H. K.; Boersma, J.; van der Meulen, J. D.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245. (b) Wilkinson, G., Ed. *Comprehensive Organometallic Chemistry*; Pergamon Press: Elmsford, NY, 1982; Vol. 16, p 830.
(32) (a) Hagen, K.; Hedberg, K.; Neisses, J.; Gundersen, G. *J. Am. Chem. Soc.* **1985**, *107*, 341. (b) Cederbal, P.; Karlsson, F. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 7.
(33) Sugiyama, K.; Shine, H. J. *J. Org. Chem.* **1983**, *48*, 143.

(Me)=O, 87367-49-5; *t*-BuN=C(H)C(Me,*t*-Bu)OH, 60294-86-2.

Supplementary Material Available: An ORTEP drawing of **1a** and tables of positional and thermal parameters for all atoms and bond lengths and bond angles of $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$ (**1a**), elemental analyses of the compounds **1a–h** and **2a–e**, and cryoscopic molecular weight determinations of various organozinc compounds in benzene (6 pages); a listing of observed and calculated structure factors for **1a** (8 pages). Ordering information is given on any current masthead page.

Reactions of Coordinated Molecules. 50. The Preparation of Homo- and Heterodinuclear Complexes Containing μ-Alkenylidene Ligands

Dawood Afzal and Charles M. Lukehart*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee

Received May 6, 1986

The formal addition of the Pt–H bond of the cationic complex $[trans\text{-}Pt(H)(PEt_3)_2(acetone)]^+$ across the C–C triple bonds of alkynyl ligands affords cationic dinuclear complexes containing bridging alkenylidene ligands. The synthesis and characterization of eight such complexes are reported. On the basis of structural data for a member complex, these molecules are believed to possess Pt–Pt, Pt–Fe, Pt–Au, Pt–W, Pt–Ni, or Pt–Pd bonds. Diagnostic spectroscopic characterization data are provided. Furthermore, a similar addition of a Pt–Me bond across an acetylide ligand also affords a dinuclear μ-alkenylidene complex.

Introduction

Cluster complexes containing hydrocarbyl fragments as bridging ligands remain of current interest to chemists because of their potential to exhibit new chemistry and their possible structural relationship to surface-bound species. Transition-metal complexes containing μ-alkenylidene ligands are one type of such compounds.[1] Recent reports demonstrate interesting chemistry at μ-alkenylidene ligands,[2] and other studies have confirmed the existence of surface-bound alkenylidene species on Pt and Pd.[3]

Bridging alkenylidene complexes have been prepared by a variety of methods (though some of these have only limited generality) such as alkyne isomerization,[4] halide displacement from *gem*-dihaloalkenes,[5] deprotonation of a μ-alkylidyne ligand,[6] metal coordination to a terminal alkenylidene ligand,[7] oxygen extrusion from diphenylketene,[8] formal dehydrogenation of ethylene,[9] nucleophilic addition to an unsaturated M–alkylidyne ligand[6e] or a $\mu\text{-}\eta^2$-acetylide ligand,[10] elimination of an alcohol from a μ-alkoxyalkylidene ligand[11] or water from μ-hydroxyalkylidene[12] and μ_3-hydroxyethylidyne[13] ligands, thermal degradation of a diruthenacyclopentenone complex,[3c,14] and the use of *N*-nitrosourethanes as a source of alkenylidene fragments.[15] The majority of these μ-alkenylidene com-

(1) Recent review: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60–128.

(2) (a) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411–413. (b) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633–1637. (c) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329–331. (d) Brum, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaun, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 966–968.

(3) (a) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978**, *15*, 407–415. (b) DeMuth, J. E. *Surf. Sci.* **1979**, *80*, 367–387. (c) Kesmodel, L. L.; Gates, J. A. *J. Electron. Spectrosc. Relat. Phenom.* **1983**, *29*, 307–312. (d) Koestner, R. J.; Frost, J. C.; Stair, P. C.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *116*, 85–103.

(4) (a) Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisinov, K. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1976**, *110*, C36–C38. (b) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obzyuk, N. S. *Ibid.* **1977**, *137*, 55–67. (c) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M.; Antipin, M. Yu.; Struchkov, Yu. *T. Ibid.* **1977**, *137*, 55–67. (d) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486. (e) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628–634. (f) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319–326. (g) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181–7183.

(5) (a) King, R. B.; Saran, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 1784–1785. (b) King, R. B.; Saran, M. S. *Ibid.* **1973**, *95*, 1811–1817. (c) King, R. B.; Saran, M. S. *Ibid.* **1973**, *95*, 1817–1824. (d) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405. (e) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329–331.

(6) (a) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862–864. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918. (c) Colburn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661–2668. (d) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680–3681. (e) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411–413. (f) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705. (g) Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1986**, *5*, 196–199.

(7) (a) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M. *J. Organomet. Chem.* **1978**, *146*, C17–C18. (b) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Aleksandrov, G. G.; Struchkov, Yu. T. *Ibid.* **1982**, *228*, 265–272. (c) Antonova, A. B.; Kovalenko, S. V.; Korniyets, E. D.; Petrovsky, P. V.; Gulbis, G. R.; Johansson, A. A. *Inorg. Chim. Acta* **1985**, *916*, 1–7.

(8) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1966**, 444–445.

(9) (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton* Trans. **1974**, 1415–1419. (b) Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1974**, 807–808.

(10) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726–2736.

(11) Awang, M. R.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091–2098.

(12) (a) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. A. *J. chem. Soc., Chem. Commun.* **1980**, 1120–1122. (b) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499–506.

(13) Seyferth, D.; Williams, G. H.; Eschbach, C. S.; Nesthe, M. O.; Merola, J. S.; Hallgren, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4867–4878.

(14) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plass, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43–C49.

(15) Herrmann, W. A.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1985**, *297*, 245–254.

0276-7333/87/2306-0546$01.50/0