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The Nature of the Reformatsky Reagent. Crystal Structure of $(BrZnCH_2COO\text{-}t\text{-}Bu{\cdot}THF)_2$

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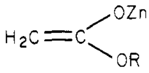
The nature of the Reformatsky reagents derived from the ethyl and *tert*-butyl esters of bromoacetic acid has been studied by association measurements and NMR spectroscopy in various solvents. It appears that the reagents are dimeric in all but the most polar solvents. A dimeric structure containing both Zn–O and Zn–C single bonds is present in the crystalline state of $(BrZnCH_2COO\text{-}t\text{-}Bu{\cdot}THF)_2$, the final X-ray analysis of which is reported. Crystals are monoclinic of space group $P2_1/n$ with two dimers in a cell of dimensions $a = 10.322$ (3) Å, $b = 12.358$ (3) Å, $c = 11.655$ (2) Å, and $\beta = 112.65$ (2)°. The structure was refined to $R = 0.055$ on 881 observed reflections with $I > 2.5\sigma(I)$. It is concluded that the dimeric structure found in the crystal persists in solution. In the very polar solvent Me_2SO, the reagents are monomeric C-metalated species. The consequences of these findings for the mechanism of the Reformatsky reaction in the commonly used solvents are discussed.

Introduction

The classic reaction between an α-bromo ester, zinc metal and a ketone, first described almost a century ago by Reformatsky,[1] is still one of the best methods for preparing β-hydroxy acids via their esters.

$$BrCH_2COOR + Zn \rightarrow \text{“}BrZnCH_2COOR\text{”} \xrightarrow[(2)\ H_2O]{(1)\ >C{=}O} >C(OH)CH_2COOR \rightarrow >C(OH)CH_2COOH$$

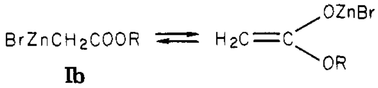
The course of the Reformatsky reaction and, in particular, its stereochemistry have been studied extensively,[2] but no clear picture has emerged as yet. One of the main reasons for this is the lack of knowledge about the nature and properties of the actual Reformatsky reagent (I). The Reformatsky reagent reacts as though it is an organozinc compound of the type "$BrZnCH_2COOR$" that adds to a carbonyl or similar group in the same way as a Grignard reagent. However, there is ample evidence that the reagent also has properties that are in accordance with an enolate type, i.e., an O-metalated structure (Ia). Thus, Vaughan et al.[3] concluded from the absence of a carbonyl group absorption in the region of 1700 cm^{-1} that the reagent occurs exclusively in the O-metalated form. They also pointed out that the Grignard reagent $Ph_2CHCH{=}C(OR)OMgBr$, which certainly is an enolate, shows a chemical behavior completely analogous to that of its zinc analogue. On the other hand, NMR studies of Gaudemar and Martin[4] and Orsini et al.[5] showed a complete absence of vinylic resonances in the ^1H NMR spectra, which was interpreted in terms of a C-metalated structure.



$H_2C{=}C(OZnBr)OR$

Ia

A complicating factor in the studies of the nature of the reagent in solution is the dependence of its spectroscopic properties on the polarity of the solvent. The changes in both IR and NMR spectra with solvent polarity have been interpreted in terms of equilibria between C-metalated (Ib) and O-metalated (Ia) species. In very polar solvents such as DMF and Me_2SO these equilibria were thought to shift to the left and it has been suggested that in the actual reaction, coordination of the substrate to the zinc occurs and that, as a consequence, the reagent would acquire the structure it has in polar solvents, i.e., the C-metalated form. As part of our studies on the coordination chemistry of functionally substituted organozinc compounds,[6] we have investigated the nature of the Reformatsky reagent both in the solid state and in solution. Part of this work has been published as a preliminary communication.[7]



$BrZnCH_2COOR \rightleftharpoons H_2C{=}C(OZnBr)OR$

Ib Ia

Experimental Section

All manipulations were carried out in an oxygen- and moisture-free nitrogen atmosphere. All solvents used were distilled from sodium/benzophenone immediately before use. The ^1H NMR spectra were recorded on Varian EM-360 and Varian EM-390 spectrometers with Me_4Si as an internal standard. Ebulliometry was performed in a Gallenkamp ebulliometer that was adapted for working in a nitrogen atmosphere. Cryometric measurements were carried out in a cryoscopic cell, which was based on a design by Dilts and Shriver[8] but used a Peltier element as a cooling device.[9] Coarsely powdered zinc (Merck; 0.3–1.5 mm)

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Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data	
formula	$C_{10}H_{19}O_3BrZn$
mol wt	332.54 (monomer)
cryst system	monoclinic-b
space group	No. 14, $P2_1/n$
a, Å	10.322 (3)
b, Å	12.358 (3)
c, Å	11.655 (2)
β, deg	112.65 (2)
V, Å^3	1372.0 (6)
Z	4 (monomers)
D_{calcd}, g/cm^3	1.61
$F(000)$	672
μ(Mo Kα), cm^{-1}	45.50
cryst size, mm	0.3 × 0.43 × 0.53
cryst volume, mm^3	0.0623
no. of grid points for abs corr	898
min and max transmissn	0.193, 0.303
b. Data Collection	
θ_{min}, θ_{max}, deg	0.1, 20
radiatn	Mo Kα (Zr filtered), 0.710 69 Å
$\omega/2\theta$ scan, deg	$0.6 + 0.35 \tan \theta$
horizontal and vertical aperture, mm	2, 6
ref reflctns	$\bar{2}30$, $0\bar{2}\bar{5}$
total data	1369
total unique	1165
obsd data ($I > 2.5\sigma(I)$)	881
total X-ray exposure time, h	1.6
c. Refinement	
no. of refined parameters	147
weighing scheme	$w^{-1} = (\sigma^2(F) + 0.012F^2)/1.12$
final $R_F = \Sigma \lvert F_o - \lvert F_c \rvert\rvert / \Sigma F_o$	0.055
final $R_{wF} = [\Sigma w(F_o - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$	0.056
rms deviation of refl on unit wt	2.57

Table II. Molecular Weight Determination of "$BrZnCH_2CO_2R$"

		R = Et		R = *t*-Bu	
solvent	method^a	mol wt (found)	degree of associatn	mol wt (found)	degree of associatn
THF	E	490	2.1	640	1.9
pyridine	E	470	2.0	650	2.0
dioxan	C	475	2.0	680	2.0
Me_2SO	C	240	1.0	355	1.1

^{a} E = ebulliometric; C = cryoscopic.

was etched with 4 N HCl, washed with water, acetone, and ether, respectively, and dried prior to use. Ethyl bromoacetate (Merck) was distilled before use. *tert*-Butyl bromoacetate was prepared from bromoacetic acid and isobutene as described by Mokosza.[10]

Preparation of the Reagents. To freshly etched zinc, an equimolar amount of ester in methylal (dimethoxymethane), or THF was added dropwise at such a rate that the solvent just gently refluxed. After the addition was completed, the reaction mixture was heated for another hour and centrifuged, and the reagent was isolated from the supernatant solution. For the ethyl reagent this was done by evaporation of the solvent (yield 75%). Anal. Calcd for $C_4H_7BrO_2Zn$: C, 20.7; H, 3.0; Br, 34.4; Zn, 28.1. Found: C, 20.7; H, 3.3; Br, 34.4; and Zn, 27.6. The *tert*-butyl reagent was isolated by concentrating the supernatant liquid, after which the reagent crystallized. The first batch of crystals (yield 30%) was used for X-ray analysis, NMR, and molecular weight measurements.

Data Collection and Structure Determination of ($BrZnCH_2COO$-*t*-Bu·THF)$_2$. A colorless block-shaped crystal, obtained by crystallization from THF, was sealed under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD4F diffractometer. Unit cell dimensions and standard deviations were determined in the usual way from the setting angles of 12 cerefully centered reflections.[11] The space group was determined as $P2_1/n$, and the data belonging to one quadrant ($+h$, $+k$, $\pm l$) were collected in the $\omega/2\theta$ scan mode, using Zr-filtered Mo Kα radiation. In a previous study of this compound, we had found that the crystals disintegrate rapidly and nonlinearly on X-ray exposure, as monitored by three reference reflections (35% during 90 h); therefore the preliminary report[7] was based on a partial data set. The structure determination reported here is based on a more rapidly collected, complete data set (θ = 20°, since reflections beyond this value tend to be very weak). The data were corrected for Lorentz and polarization effects and absorption in the previously described way.[11] No correction for decay was found necessary in this case since the two sets of reference reflections agreed within 1%. Details of the data collection and structure determination are summarized in Table I.

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares methods. Hydrogen atoms were introduced on calculated positions and refined in the riding mode on their carrier atoms. All non-hydrogen atoms were assigned anisotropic thermal parameters. The THF hydrogen atoms were assigned a thermal parameter of 0.1 Å^2; the CH_2 and *t*-Bu groups were each assigned one variable isotropic hydrogen thermal parameter. The refinement converged at R_F = 0.055 (R_{wF} = 0.056) for 147 parameters and 881 observed reflections with $I > 2.5\ \sigma(I)$. In the final structure, the THF ring appears to be nearly planar. We believe that this is an artifact caused by disorder of the THF ligands in the crystal. The THF molecule preferentially adopts a twisted conformation with a twofold axis through the oxygen atom.[12] A superposition of two such conformations, related by a mirror plane through the ring, would produce the image we find here. In accord with this explanation, the thermal parameters of the THF carbon atoms have an abnormally large amplitude perpendicular to the ring plane. In view of the limited resolution of the data set, we did not attempt to refine any disorder models; in any case, the precise conformation of the THF ligand was not considered to be very relevant. Neutral atom scattering factors were taken from ref[13] and corrected for anomalous dispersion.[14] All calculations were carried out on the Cyber 175 of the University of Utrecht Computer Centre. Programs used include SHELX-76 (structure refinement[15]), PLATO (geometry analysis[16]), and ORTEP (plotting program[17]).

Results

A notable shortcoming in all studies of the Reformatsky reagent reported so far is the absence of (molecular) association measurements. It is to be expected that in all but the most polar solvents, the reagent, no matter what its structure really is, will be associated into dimers or higher associates in order to reach coordination saturation of the zinc. Therefore, we have employed molecular weight measurements to determine the degree of association of the Reformatsky reagents derived from both the ethyl and the *tert*-butyl ester of bromoacetic acid. The measure-

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Table III. ^{1}H Chemical Shifts of the Reformatsky Reagents in Ppm Relative to Internal Me_4Si^a

$\mathrm{BrZn\underset{a}{CH_2}CO_2\underset{b}{CH_2}\underset{c}{CH_3}}$ $\mathrm{BrZn\underset{d}{CH_2}CO_2C(\underset{e}{CH_3})_3}$

solvent^b	a	b	c	d	e
methylal	1.97 (2.00)	4.11 (4.14)	1.24 (1.22)	c	c
THF	2.10	4.1^d	1.27	2.00 (1.88)	1.47 (1.40)
DME	1.95 (1.93)	4.1^d (4.09)	1.27 (1.21)	1.82	1.47
dioxan	1.97 (1.89)	4.13 (4.07)	1.27	1.80	1.50
pyridine	1.94	4.05	1.05	2.13 (2.00)	1.43 (1.46)
HMPT	1.20 (1.21)	3.83 (3.80)	1.08 (1.10)	1.15	1.33
Me_2SO	1.15 (1.17)	3.80 (3.82)	1.03 (1.04)	1.10 (1.04)	1.33 (1.30)

^{a} Literature values are given in parentheses. Values are taken from ref 4 for $BrZnCH_2CO_2Et$ and from ref 5 for $BrZnCH_2CO_2$-*t*-Bu. ^{b} THF = tetrahydrofuran; DME = dimethoxyethane; HMPT = hexamethylphosphorous triamide; Me_2SO = dimethyl sulfoxide. ^{c} Not determined because of poor solubility. ^{d} Partially obscured by solvent peaks.

Table IV. Fractional Atomic Coordinates for the Non-Hydrogen Atoms and Equivalent Isotropic Temperature Factors

atom	*X/a*	*Y/b*	*Z/c*	*U*(eq),^{a} Å^2
Br(1)	0.0857 (2)	0.0609 (1)	0.2464 (2)	0.07
Zn(1)	0.0747 (2)	0.1141 (1)	0.4357 (2)	0.05
O(11)	0.114 (1)	0.2770 (9)	0.444 (1)	0.08
O(21)	0.129 (1)	−0.1356 (8)	0.5911 (9)	0.05
O(24)	0.334 (1)	−0.0825 (7)	0.5865 (9)	0.05
C(12)	0.195 (3)	0.336 (2)	0.541 (2)	0.11
C(13)	0.209 (3)	0.444 (2)	0.494 (3)	0.15
C(14)	0.111 (3)	0.450 (2)	0.369 (2)	0.12
C(15)	0.058 (3)	0.344 (2)	0.339 (2)	0.16
C(22)	0.214 (2)	−0.056 (1)	0.595 (1)	0.05
C(23)	0.183 (2)	0.055 (1)	0.603 (1)	0.06
C(25)	0.368 (2)	−0.190 (1)	0.552 (2)	0.07
C(26)	0.255 (1)	−0.225 (1)	0.431 (2)	0.08
C(27)	0.392 (2)	−0.267 (1)	0.659 (2)	0.09
C(28)	0.506 (2)	−0.165 (2)	0.536 (2)	0.10

^{a} $U_{eq} = {}^1/_3\ \Sigma_{ij} U_{ij} a_i{}^* a_j{}^* \vec{a}_i \vec{a}_j$.

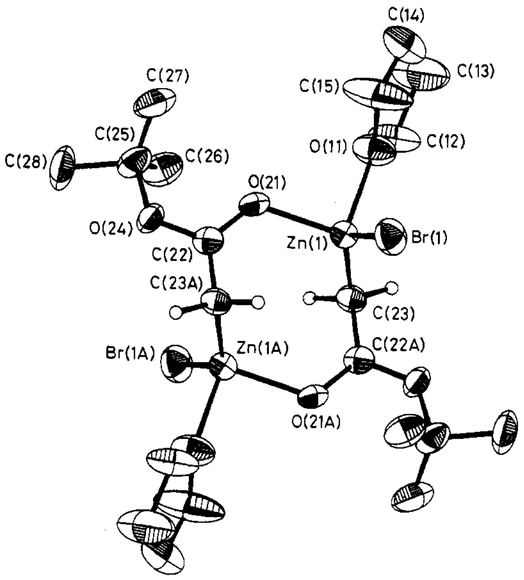


Figure 1. ORTEP drawing of a ($BrZnCH_2COO$-*t*-Bu·THF)$_2$ dimer showing 40% probability ellipsoids. The hydrogen atoms of the *tert*-butyl and the THF ligand have been omitted for clarity. The symbol A denotes the symmetry operation (−*x*, −*y*, 1 − *z*).

ments were carried out in a series of solvents that are normally used in the Reformatsky reaction. Although it would have been interesting to include noncoordinating solvents such as aliphatic and aromatic hydrocarbons, the extremely poor solubility in these solvents precluded this.

The ethyl ester derivative could be isolated in solvent-free form from dimethoxymethane, but the *tert*-butyl ester derivative, which was prepared in THF, still contained one THF molecule per zinc atom. This complicates the molecular weight measurements of the latter compound, since upon dissolution, in particular in a more polar solvent, the coordinated THF is liberated and adds to the number of molecules present in solution. Therefore, a correction becomes necessary. The results, corrected for the release of THF, are presented in Table II. In no case was any concentration dependence observed. It appears that the normal mode of association of the reagent is dimeric. Only in the very polar solvent Me_2SO is a monomeric state found. Remarkably, pyridine, which is normally able to cleave organozinc associates, does not do so in this case. These results also indicate that the nature of the ester group in the reagent apparently has no influence on its degree of association in solution.

Some NMR data of both Reformatsky reagents covered in this paper have been recorded earlier.[4,5] To allow a correlation between the degrees of association and the NMR data, we have extended the NMR measurements to the solvents used in the molecular weight determination. The results are given in Table III.

In view of the fact that in solution dimeric association appeared to be the preferred state of the reagent, persisting even in a polar solvent like pyridine, it seemed very likely that this dimeric state also occurs in the solid state. The report of Orsini et al.[5] on the crystallinity of the reagent derived from the *tert*-butyl ester of bromoacetic acid prompted us to determine the crystal structure of this reagent. The compound forms monoclinic crystals, with two dimeric units in the unit cell. Figure 1 shows an ORTEP

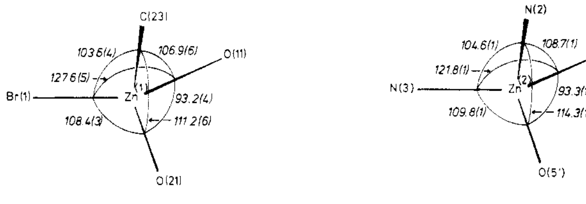
Table V. Selected Bond Distances (Å) and Angles (deg)

(a) Bond Distances

Br(1)-Zn(1)	2.346 (3)	C(25)-C(26)	1.51 (3)	C(22)-C(23A)	1.41 (2)
Zn(1)-O(21)	2.02 (1)	C(25)-C(28)	1.54 (3)	O(24)-C(25)	1.47 (2)
O(21)-C(22)	1.31 (2)	Zn(1)-O(11)	2.05 (1)	C(25)-C(27)	1.51 (3)
O(24)-C(22)	1.32 (2)	Zn(1)-C(23)	1.98 (2)		

(b) Bond Angles

Br(1)-Zn(1)-O(11)	103.6 (4)	O(11)-Zn(1)-C(23)	106.9 (6)	O(21)-C(22)-C(23A)	125 (1)
Br(1)-Zn(1)-O(21)	108.4 (3)	O(21)-Zn(1)-C(23)	111.2 (6)	O(24)-C(22)-C(23A)	119 (1)
Br(1)-Zn(1)-C(23)	127.6 (5)	Zn(1)-O(21)-C(22)	123 (1)	O(21)-C(22)-O(24)	116 (1)
O(11)-Zn(1)-O(21)	93.2 (4)	C(22)-O(24)-C(25)	125 (1)	Zn(1)-C(23)-C(22A)	110 (1)



(I) (II)

Figure 2. Comparison between bond angles in ($BrZnCH_2COO$-t-$Bu{\cdot}THF)_2$ (I) and $Et_2Zn_4(NPhCOOMe)_6{\cdot}2C_6H_6$ (II).

drawing of a dimeric unit with the adopted numbering scheme. A selection of bond distances and bond angles is given in Table V.

The dimeric unit, with a crystallographically imposed center of symmetry, consists of a nonplanar eight-membered $(ZnCCO)_2$ ring. The two zinc atoms are surrounded in a roughly tetrahedral fashion by a coordinated THF molecule, a bromine atom, a carbon atom, and an oxygen atom. The bond angles around the zinc are nearly equal to those around Zn(2) in the ethylzinc derivative of *N*-phenylmethylcarbamate[11] (cf. Figure 2). The fact that the length of the zinc–carbon bond (1.98 (2) Å) is close to that in ethylzinc iodide (1.95 (4) Å),[18] methylzinc methoxide (average value 1.95 Å),[19] and dimethylzinc (1.94 Å)[20] indicates that it is a normal zinc–carbon single bond. The Zn–O(21) distance of 2.02 (1) Å is comparable to the nonbridging zinc–oxygen bonds in $Ph_2Zn_3Acac_4$ (average value 2.005 Å)[21] and shorter than those in methylzinc methoxide (shortest bond length 2.039 (15) Å, average value 2.087 Å).[19] This bond, therefore, must be regarded as a normal single zinc–oxygen bond. The dative bond between THF and zinc (2.05 Å) is rather short but lies within the range of other reported zinc–oxygen coordinate bonds (2.12 Å for acetone,[22] 2.11 Å for THF,[23] and 2.07 Å for DME[24]).

Discussion

The crystal structure determination clearly shows, that, at least in the solid state, the Reformatsky reagent cannot realistically be described in terms of either C-metalated or O-metalated species. Both the zinc–carbon and the zinc–oxygen bonds in the dimer are normal single bonds. Another structural feature of the *tert*-butyl derivative is the preference of THF coordination over Zn–Br–Zn bridging. The occurrence of the latter, which would cause association to higher aggregates, might well be impeded by the presence of the two relatively bulky *tert*-butyl groups. The THF in this compound is quite strongly bound, as indicated both by the rather short Zn–O coordinate bond length and by the fact that the compound cannot be freed from THF by evacuation at ambient temperature.

The study of the Reformatsky reagent in solution is somewhat complicated by the presence of Schlenk equilibria (eq 1 and 2). The occurrence of these equilibria is

$$2BrZnCH_2COOR \rightleftarrows ZnBr_2 + Zn(CH_2COOR)_2 \qquad (1)$$

$$(BrZnCH_2COOR)_2 \rightleftarrows ZnBr_2 + 1/n[Zn(CH_2COOR)_2]_n \qquad (2)$$

shown by the fact that, when pentane is added to a solution of a Reformatsky reagent in pyridine or Me_2SO, a precipitate is formed that was identified as the $ZnBr_2$ complex of pyridine or Me_2SO, respectively. A complex of $ZnBr_2$ is also isolated when 2,2′-bipyridine is added to a Reformatsky reagent.[25] We observed that the Reformatsky reagent is a dimer in all but the most polar solvents. This means that eq 2 applies in these solvents. For all values of n, the apparent degree of association will be less than 2 if eq 2 is not completely to one side. The observed dimeric state of the reagent thus indicates that this equilibrium lies completely to the left. In the strongly coordinating solvent Me_2SO, a monomeric state of the reagent was found. If in this solvent equilibrium 1 exists, molecular weight determination cannot distinguish between the monomer and the disproportionated products, since the number of particles in solution does not change.

The ^1H NMR spectra of both reagents show great similarity in the chemical shifts of the CH_2 group bound to zinc. In all solvents in which the reagent was found to be a dimer the CH_2 resonances are found between 1.8 and 2.1 ppm. In Me_2SO, where the reagent is monomeric, a high-field shift of about 0.8 ppm is observed. These facts were interpreted earlier by Gaudemar and Martin[4] and Orsini et al.[5] in terms of the presence of the C-metalated form of the reagent in very polar solvents. Our results are in agreement with this interpretation. The low-field position of the CH_2 resonance in the dimer will be caused by the presence of coordinate bonds between the carbonyl groups and the zinc atoms. In solvents like Me_2SO, this coordination is broken and a solvated, monomeric, C-metalated species is formed. Also the IR data reported earlier by Gaudemar and Martin[4] are in accordance with solvent-dependent association. In all solvents in which the reagent is dimeric, the main carbonyl vibration is found at a low wavenumber, due to weakening of the carbonyl bond upon formation of the zinc–oxygen coordinate bond. In strongly polar solvents the main carbonyl group vibration is found just below 1700 cm^{-1}, which is the normal value for ester carbonyl groups.

As was first stated clearly by Seebach et al.[26] for the reaction of lithium enolates, the aggregation state of an organometallic reagent will have mechanistic implications for its reaction with organic substrates. Therefore, in a mechanistic discussion of the Reformatsky reaction, the dimeric nature of the reagent in the solvents commonly used in the reaction must be taken into consideration. A model study shows that after the first step, which will be displacement of a solvent molecule by the carbonyl group of the substrate, the reagent–substrate complex may react further in two ways: either in a four-center mechanism or in a six-center mechanism. The latter mechanism is clearly to be preferred for steric reasons.[7] This model can also be used to visualize the consequences of modifications in the reagent. Changes in the ester moiety should hardly affect the reaction. This is indeed the case, as shown by Newman and Evans.[27] Even large ester groups do not inhibit the reaction, since both *p*-methylphenyl bromo-

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acetate and *p*-chlorophenyl bromoacetate can be used. On the other hand, substitution of the hydrogen atoms on the α-carbon atom will increase steric hindrance. In a series of experiments, Hussey and Newman[28] showed that the yield of β-hydroxy esters dropped when the α-hydrogens were replaced by methyl groups. They attributed this to enolization of the ketone and subsequent reaction of the reagent with the enol form of the ketone. Apparently, this side reaction becomes more important with increased branching of the α-carbon.

All available evidence thus indicates that the Reformatsky reagent is a monomeric, C-metalated species (Ib) in strongly polar solvents and a dimer with bridging $CH_2C(OR)O$ groups in all other solvents.

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Registry No. $(BrZnCH_2COO\text{-}t\text{-}Bu\cdot THF)_2$, 90528-93-1; $BrZnCH_2COOEt$, 5764-82-9.

Supplementary Material Available: Tables of all positional and thermal parameters and bond lengths and bond angles and a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Binuclear Phosphido-Bridged WPt, WPd, and WNi Complexes. Crystal and Molecular Structures of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Pt}(PPh_3)$ and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Pt}\{CH_3O_2CC{\equiv}CCO_2CH_3\}$

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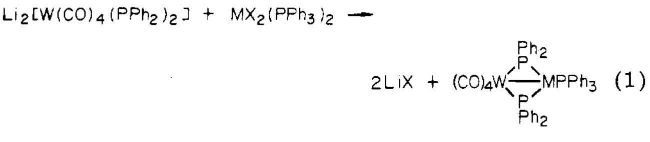
The new complexes $(CO)_4\overline{W(\mu\text{-}PPh_2)_2M}(PPh_3)$ (M = Pt, **1**, Pd, **2**, and Ni, **3**) have been prepared by reaction of $Li_2[W(CO)_4(PPh_2)_2]$, generated in situ, with the corresponding $MCl_2(PPh_3)_2$ complex. These complexes have been spectroscopically characterized with the WPt complex **1** further defined by an X-ray diffraction study. It crystallizes in the space group $P2_1/c$ with $a = 11.672$ (2) Å, $b = 18.726$ (3) Å, $c = 19.869$ (3) Å, $\beta = 96.08$ (1)°, $V = 4317$ (1) Å^3, and $Z = 4$. The structure has been refined for the 4491 reflections with $(F_o) > 3\sigma(F_o)$ to R and R_w values of 0.0505 and 0.0495. The W and Pt atoms are bridged by two μ-PPh_2 ligands and joined by a metal–metal bond (2.764 (1) Å). The W is further coordinated by four CO's and the Pt by a PPh_3 ligand. Similar structures are indicated for **2** and **3**. Complexes **1** and **2** show no appreciable reaction with H_2 nor CO under moderate pressures but do react with activated alkynes to quantitatively yield $(CO)_4\overline{W(\mu\text{-}PPh_2)_2M}(MeO_2CC{\equiv}CR)$ (M = Pt, R = CO_2Me, **4**; M = Pt, R = H, **5**; M = Pd, R = CO_2Me, **6**) in which the alkyne has replaced the PPh_3 ligand. Complex **4** crystallizes in the space group $P2_1/n$ with $a = 11.438$ (4) Å, $b = 11.095$ (4) Å, $c = 17.764$ (6) Å, $\beta = 95.55$ (2)°, $V = 3457$ (2) Å^3, and $Z = 4$. The structure refined for the 4098 reflections with $(F_o) > 2.5\sigma(F_o)$ to $R = 0.0431$ and $R_w = 0.0336$. The structure is similar to that of **1** with the alkyne coordinated to Pt such that the alkyne ligand lies nearly in the plane defined by Pt and the two bridging phosphorus atoms. Details of the reaction of **1** with HBF_4 and HCl are also reported.

Heterobimetallic complexes that combine metals with different sets of chemical properties are inherently interesting because they may lead to unusual substrate activation and perhaps unique catalytic chemistry.[1] Particularly interesting are complexes that link metals in groups 4–6 with those in group 8, especially the more active latter metals that readily undergo oxidative-addition/reductive-elimination reactions and which are of catalytic relevance. In other work,[2] we have described such phosphido-bridged WOs, WRh, and WIr complexes, and herein we report new derivatives which link W to Ni, Pd, and Pt, prepared by the general reaction of eq 1. The chemistry of these complexes has been briefly explored, particularly their reactions with alkynes. Also reported are the crystal and molecular structures of complex **1** and its $MeO_2CC{\equiv}CCO_2Me$ derivative, $(CO)_4\overline{W(\mu\text{-}PPh_2)Pt}(MeO_2CC{\equiv}CCO_2Me)$.



1, M = Pt
2, M = Pd
3, M = Ni

Experimental Section

$W(CO)_4(PPh_2H)_2$,[2b,3] *cis*-$PtCl_2(PPh_3)_2$,[4] $PdCl_2(PPh_3)_2$,[5] and

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