

NEW ASPECTS OF METAL CARBONYL YLIDE CHEMISTRY*

E. LINDNER

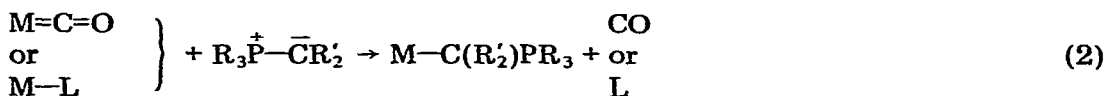
Institut für Anorganische Chemie der Universität Tübingen, Tübingen (B.R.D.)

The known reactions of phosphorus ylides with metal carbonyls can be classified on principle into two reaction types:

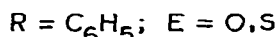
(1) Wittig analogous reactions with terminal carbon monoxide groups (eqn. 1). In these reactions intermediary adducts of the Wittig reaction can be isolated from the metal carbonyl and the ylide as Kaska has already shown.



(2) Ligand displacement by the ylide is possible (eqn. 2), in the course of which the carbon atom which is in an α -position with respect to the phosphorus atom acts as a σ -donor.



The ylides we are concerned with, namely carbonylmethylene- and thiocarbonylmethylene-triphenylphosphorane and bis(phenylmercapto)methylenetriphenylphosphorane are sp^2 and sp^3 hybridized at the linking carbon atom. Their basicity however is not sufficient enough in both cases to give Wittig analogous reactions. Their basic character could be increased especially, the bis(organylmercapto)methylenetriphenylphosphorane, by introduction of electron-donating organic residues ($\text{R} = \text{CH}_3$).



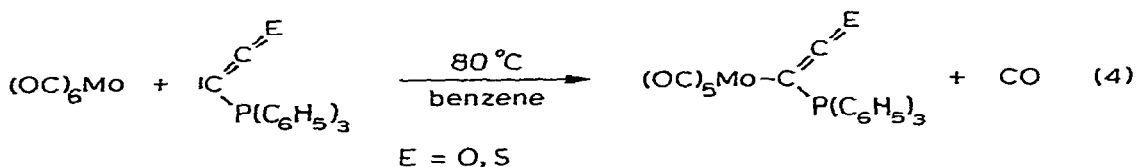
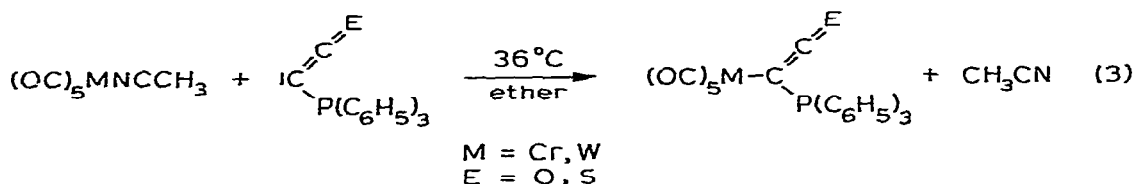
* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

TABLE 1
SOME CHARACTERISTIC PROPERTIES OF GROUP VI METAL YLIDE COMPLEXES

Compound	M.p. (°C) dec.	Colour	Solubility
(OC) ₅ CrC[P(C ₆ H ₅) ₃]CO	146	Yellow	Soluble in
(OC) ₅ MoC[P(C ₆ H ₅) ₃]CO	105	Light yellow	all polar
(OC) ₅ WC[P(C ₆ H ₅) ₃]CO	145	Yellow	solvents,
(OC) ₅ CrC[P(C ₆ H ₅) ₃]CS	162	Orange	partially
(OC) ₅ MoC[P(C ₆ H ₅) ₃]CS	100	Yellow	soluble in
(OC) ₅ WC[P(C ₆ H ₅) ₃]CS	84	Yellow	nonpolar
			solvents

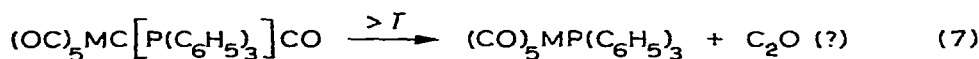
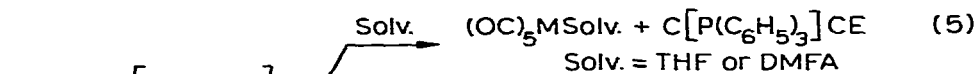
Following is a report on the reactions of the ylide ligands shown in Table 1 with Group VI hexacarbonyls which were investigated by our group.

For the case of carbonylmethylenetriphenylphosphorane the chromium and tungsten compounds were prepared from the corresponding pentacarbonyl-acetonitrilemetal complexes (eqn. 3), the molybdenum compound however is better obtained thermally in benzene at 80°C (eqn. 4).



Some important properties of these ylide complexes, their elemental analyses, molecular weight determinations, mass spectra and IR spectra are shown in Table 1. They melt under decomposition at the given temperatures and have been found to be surprisingly stable with the exception of the molybdenum compound. All complexes are readily soluble in polar solvents and partially soluble even in nonpolar solvents. In solution however they decompose after a relatively short time. Thus the ligand is easily exchanged by polar solvents such as tetrahydrofuran or dimethyl formamide (eqn. 5) as shown by time dependent IR investigations. The ylide ligands evidently have only little π -acceptor properties which can also be concluded from the IR spectra (see later). In the case of the chromium and molybdenum complexes in less polar solvents like carbon tetrachloride (eqn. 6) chromium hexacarbonyl and molybdenum hexacarbonyl as well as unidentified products are formed. With the more stable tungsten complex this effect can only be observed above 50°C. The corresponding thio compounds behave similarly. The phosphine substituted compounds (OC)₅MP-(C₆H₅)₃ are formed in good yields, together with a little hexacarbonyl, when

the carbonylmethylenetriphenylphosphorane complexes are heated between 100 and 110°C (eqn. 7). The formation of $(OC)_5MP(C_6H_5)_3$ however should result in the liberation of carbonylmethylene. Our further efforts therefore were directed towards detection of the carbene C_2O and to investigate its complex chemical properties.



for $M = W$: $\nu(C-O) = 2073 m, 1985 w, 1945 vs$ solv. CCl_4

In Table 2 are shown some characteristic IR frequencies of the ylide ligands and both tungsten complexes. The spectra of the chromium and molybdenum compounds are similar. In the carbonyl- and thiocarbonyl-methylenetriphenylphosphorane the C_2O and C_2S groups respectively are characterized above all by two absorptions which correspond to the asymmetric and symmetric C_2O and C_2S stretching vibrations. When the ligands are coordinated to the metals, $\nu_{as}(C_2O)$ is shifted to lower frequencies by approximately 20 cm^{-1} . Similarly, this can also be expected for $\nu_{as}(C_2S)$, but this band is obscured by the intensive twofold degenerate $\nu(C-O)$ absorption. Also $\nu_s(C_2S)$ could not be assigned in the spectrum of the complexes. The shift to lower wavelengths of the $C-O$ stretching vibrations indicates that the ylide ligands have only little π -acceptor properties.

In a similar way the bis(phenylmercapto)methylenetriphenylphosphorane complexes of chromium and tungsten are also obtained directly or indirectly photochemically. Some important properties like melting points, colours, solubilities and molecular weight determinations are summarized in Table 3. Toward polar and nonpolar solvents the bis(phenylmercapto)methylenetri-

TABLE 2

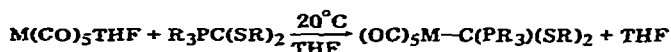
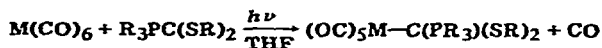
$\nu(C-O)$, $\nu_{as}(C_2E)$ and $\nu_s(C_2E)$ STRETCHING VIBRATIONS OF $(H_5C_6)_3PC_2E$ AND $(OC)_5WC[P(C_6H_5)_3]CE$ ($E = O, S$)

(The corresponding absorptions of the chromium and molybdenum compounds are very similar)

Compound	$\nu(C-O)$	$\nu_{as}(C_2E)$	$\nu_s(C_2E)$	Phase
$(H_5C_6)_3PC_2O$		2104vs	1312m	Solid KBr
$(H_5C_6)_3PC_2S$		1975vs	751m?	Solid KBr
$(OC)_5WC[P(C_6H_5)_3]CO$	2058m-s(A_1) 1953(sh)(B_1) 1928vs(E) 1903s(A_1)	2084m-s	1311m	Sol. CCl_4
$(OC)_5WC[P(C_6H_5)_3]CS$	2050m(A_1) 1931vs(E) 1901m-s(A_1)	Obs.	Obs.	Sol. CCl_4

TABLE 3

PROPERTIES OF BIS(PHENYLMERCAPTO)METHYLENETRIPHENYLPHOSPHORANE COMPLEXES OF GROUP VI METAL CARBOXYLS

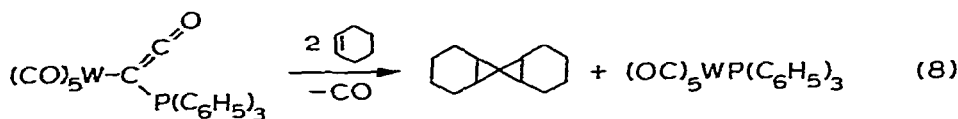


M = Cr, W; R = C₆H₅

	M.p. (°C) (dec.)	Colour	Solubility	Mol. wt. (in benzene)
M = Cr	118	Yellow	Soluble in all polar solvents, partially soluble in nonpolar solvents	698(684)
M = W	120	Dark yellow		947(893)

phenylphosphorane complexes behave similarly to the carbonylmethylenetriphenylphosphorane complexes; that is, they undergo CO disproportionation or ligand exchange.

From the ³¹P NMR spectra (Table 4) it follows unequivocally that the triphenylphosphine residue of the ylide ligand was not separated during the reaction and that the ligand is linked via the carbon atom to the metals. In the IR spectra there appear again 4 C—O absorptions in the 5μ region (for a discussion of these results see later). The mass spectra of both the ylide complex species are characterized by thermolysis reactions. Among others one always observes the fragments (OC)₅MP(C₆H₅)₃ and the carbenes carbonylmethylene, thiocarbonylmethylene and bis(phenylmercapto)methylene.



7,7-Spirobinorcarane

Mass spectrum: mol. peak $m/e = 176$

IR spectrum: no olefinic $\nu(C-H)$

no C=C absorptions

¹H NMR spectrum: peaks in the region $\tau = 8-9$ ppm

Elemental analysis

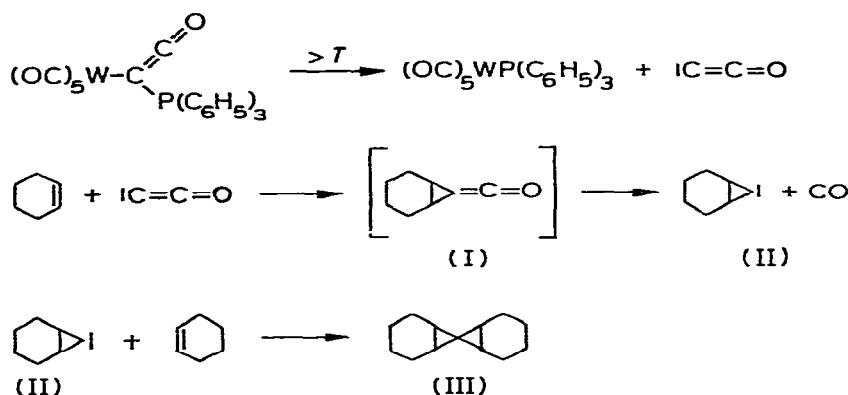
We allowed the tungsten complex to react with cyclohexene at 110°C (eqn. 8) and isolated after chromatography (OC)₅WP(C₆H₅)₃ and 7,7'-spirobinorcarane. The latter was detected by mass, IR and ¹H NMR investigations as well

TABLE 4

³¹P NMR DATA OF R₃P—C(SR)₂ AND (OC)₅M—C(PR₃)(SR)₂ (R = C₆H₅; M = Cr, W) (H₃PO₄ STANDARD)

R ₃ P—C(SR) ₂	−25.6 ppm	Sol. in CCl ₄
(OC) ₅ Cr—C(PR ₃)(SR) ₂	−28.1 ppm	Sol. in C ₆ H ₆
(OC) ₅ W—C(PR ₃)(SR) ₂	−27.9 ppm	Sol. in C ₆ H ₆

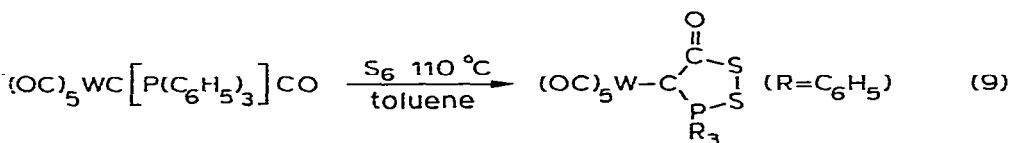
SCHEME 1



as elemental analysis. We assume the course of reaction in Scheme 1. The carbonylmethylene, eliminated by thermolysis of the tungsten ylide complex, reacts with cyclohexene to form the unstable intermediate cyclohexenylketene (I) which is converted to the carbene II by CO elimination. With excess cyclohexene, II reacts to give the spiro compound III.

Our further interests were directed toward the question of whether it was possible to separate triphenylphosphine from the respective ylide complexes without attacking the metal-carbon bond and obtain the carbene complexes $(\text{OC})_5\text{MC}_2\text{O}$ and $(\text{OC})_5\text{MC}(\text{SR})_2$, respectively.

We allowed some ylide complexes to react with the reactive cyclohexasulfur, to eliminate triphenylphosphine as triphenylphosphine sulfide. After reaction at 110°C in toluene followed by chromatography one obtains a reaction product, in which the P-C linkage is preserved and a cyclisation with two sulfur atoms takes place. We obtained a monomeric orange carbene complex (eqn. 9) identified on the basis of its mass spectrum, molecular weight determinations,



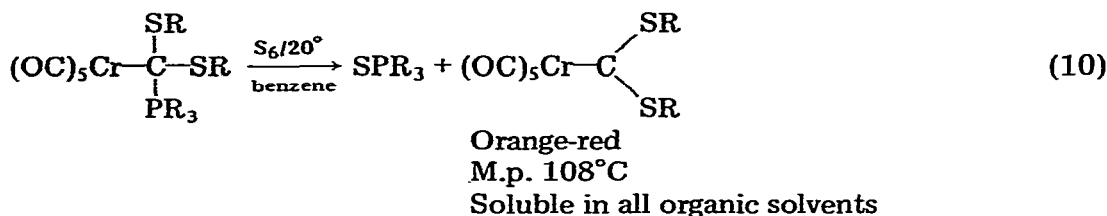
$\nu(\text{C}-\text{O})$:	Orange
2078 m (A_1)	Carbene complex
1985 w-m (B_1)	M.p. 159-161°C (dec.)
1935 vs (E)	Some fragments in the mass spectrum
1895 s (A_1)	
$\nu(>\text{C}=\text{O})$:	$\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$
1618 m	$(\text{H}_5\text{C}_6)_3\text{PC}_2\text{O}$
$\nu(\text{C}-\text{S})$:	$(\text{H}_5\text{C}_6)_3\text{PS}$
631 w ?	OCS_2
$\nu(\text{S}-\text{S})$ (IR): 472 w	C_2S
(Raman): 481 s	CS
	COS

TABLE 5
 $\nu(\text{C—O})$ IR DATA OF THE YLIDE AND CARBENE COMPLEXES

Compound	$\nu(\text{C—O})$	Solvent
$(\text{OC})_5\text{Cr—C}(\text{PR}_3)(\text{SR})_2$	2065m(A_1), 1987m(B_1) 1942sst(E), 1917st(A_1)	CCl_4
$(\text{OC})_5\text{W—C}(\text{PR}_3)(\text{SR})_2$	2070m(A_1), 1983m(B_1) 1939sst(E), 1915st(A_1)	CCl_4
$(\text{OC})_5\text{Cr—C}(\text{SR})_2$	2065m-st(A_1) 1954sst(E) 1936st(A_1)	n-hexane

elemental analysis as well as IR and Raman spectra. If however the reaction proceeds at lower temperatures there results a yellow complex which in the infra-red shows only three absorptions for $\nu(\text{C—O})$ (2060, 1950, 1935 cm^{-1}) and one for the ketonic carbonyl stretching vibration at 1860 cm^{-1} (free C_2O ligand: 1978, 1074, (1048), 381). At the moment we are not yet very sure (because it is a very recent result), but it may be that we have isolated the hitherto unknown carbene complex $(\text{OC})_5\text{WC}_2\text{O}$. Further investigations of course have to be carried out.

If one allows cyclohexasulfur to react with pentacarbonyl[bis(phenylmercapto)methylenetriphenylphosphorane]chromium in benzene under mild conditions at room temperature, one obtains the orange-red pentacarbonyl[bis(phenylmercapto)carbene]chromium by elimination of triphenylphosphine sulfide (eqn. 10). The yields of this relatively stable compound are about 15% and can certainly be increased. It melts at 108°C and is soluble in all organic solvents.



The fact that a carbene complex was produced here, is shown by the IR spectrum (Table 5). The C—O stretching vibrations are shifted to higher frequencies compared with those of the corresponding ylide complex, which can be traced back to the better π -acceptor properties of the carbene ligand. In contrast to the four peaks in the spectra of the ylide complexes there appear only three bands ($2A_1 + E$) because of the less distorted C_{4v} symmetry. Our further investigations now will be focused on preparation of a better C_2O generator and to determine how general Wittig analogous reactions with the ylide ligand bis(organylmercapto)methylenetriphenylphosphorane are possible when the organic residue R is varied.