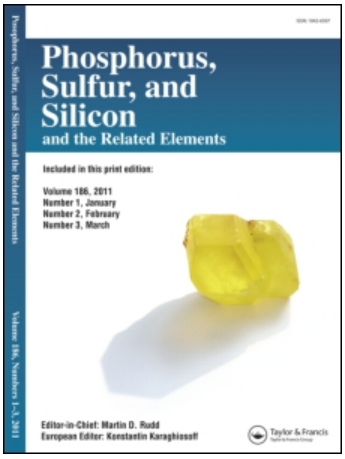

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Complexes wits a Thioalkyl-Bridged M-P-Bond from Metallo(Alkylthio)Phosphanes

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COMPLEXES WITH A THIOALKYL-BRIDGED M-P-BOND FROM METALLO(ALKYLTHIO)PHOSPHANES

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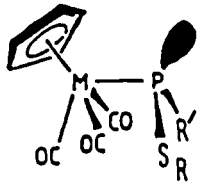
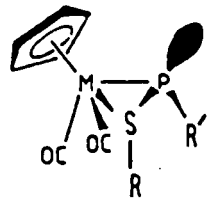
Metallation of alkylthio(chloro)phosphanes ClP(R')S-R (R = i-Pr, tBu; R' = tBu, St-Bu) and Cl_2P-S-tBu with $Na[M(CO)_3Cp]$ (M = Cr, Mo, W) yields the metallo-(alkylthio)chloro-, metallo-bis(alkylthio)-, metallo-(alkylthio)(alkyl)phosphanes (1a-f) or the bis(metallo)(alkylthio)phosphane (1g) respectively.



1	a	b	c	d	e	f	g
R	tBu	tBu	tBu	tBu	tBu	tBu	tBu
R'	Cl	Cl	StBu	StBu	StBu	tBu	$Cp(CO)_3W$
M	Mo	W	Cr	Mo	W	W	W



2	a	b	c	d	e	f	g	h
R	tBu	tBu	tBu	tBu	iPr	tBu	tBu	tBu
R'	tBu	StBu	StBu	$Cp(CO)_3W$	tBu	tBu	$Cp(CO)_3Mo$	$Cp(CO)_3W$
M	W	Mo	W	W	Mo	Mo	Mo	Mo

Due to the bulkiness of the P-bonded non metal ligands the metallo-(alkylthio)phosphanes 1d-g can be easily decarbonylated either thermally or via reaction with $Ni(CO)_4$ to give the metallacycles 2a-d . 2e,f / 2g,h are obtained directly from $Na[Mo(CO)_3Cp]$ and the chlorophosphines / 1a,b. 2a-h represent a valence tautomer of the originally expected metal to phosphorus double bonded species $Cp(CO)_2M{=}P(R')SR$. The proposed structure of 2h is proved by reaction with Li-S-iPr yielding 2b. The combination of a thioalkyl ligand with a bulky amino- or phenoxy group preferentially yields the M=P-isomer. This fact is demonstrated by the generation of $Cp(CO)_2W{=}P(R)S$-iPr from $Cp(CO)_2W{=}P(R)Cl$ (R = 2.2.6.6 tetramethylpiperidyl, 2.6. di(tert.butyl)phenoxy) and Li-S-iPr.