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Molybdenum-95 Nuclear Magnetic Resonance of a Series of Phosphine and Phosphite Substituted Molybdenum Carbonyls $Mo(CO)_{6-n}(L)_n$ (n = 1, 2, 3, 4, 5)

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Molybdenum-95 NMR spectra of a series of phosphine and phosphite substituted molybdenum carbonyls $Mo(CO)_{6-n}L_n$ [$L = P(OCH_3)_3$ $n = 1, 2, 3, 4, 5$, $L = P(OC_2H_5)_3$ $n = 1, 2, 3$, $L = P(C_6H_5)_3$ $n = 1$] including isomers (*cis*, *trans*, *fac*, *mer*) are reported. A large range of chemical shifts is found for the title compounds. The coupling constants $^1J(^{95}Mo\text{-}^{31}P)$ are derived either from ^{95}Mo-NMR spectra or ^{31}P-NMR spectra. Syntheses of the measured compounds were performed by thermal or photochemical ligand substitution.

(Keywords: Coupling constants, 95 Mo—31 P; Mo-95-*NMR*; P-31-*NMR*)

Molybdän-95 NMR einer Reihe von Phosphin- und Phosphit-substituierten Molybdäncarbonylen $Mo(CO)_{6-n}(L)_n$ *(n = 1, 2, 3, 4, 5)*

Es werden die ^{95}Mo-NMR-Spektren der im Titel genannten Verbindungen mit $L = P(OCH_3)_3$ $n = 1$—5, $L = P(OC_2H_5)_3$ $n = 1$—3 und $L = P(C_6H_5)_3$ $n = 1$, einschließlich von Isomeren (*cis*, *trans*, *fac*, *mer*) angegeben. Für die chemischen Verschiebungen wurde ein sehr weiter Bereich beobachtet. Die Kopplungskonstanten $^1J(^{95}Mo\text{-}^{31}P)$ wurden entweder von den ^{95}Mo- oder ^{31}P-NMR-Spektren ermittelt. Die Synthese der Verbindungen erfolgte mittels thermischem oder photochemischem Ligandenaustausch.

We wish to report the ^{95}Mo-NMR chemical shift and spectra we obtained of a series of substituted molybdenum carbonyl species at natural abundance (15.8 atom%) with a Bruker WP 80 NMR spectrometer operating in the pulsed *Fourier* Transform mode at 1.88 T. All samples were measured at 31 °C. Thermal ligand substitution till the $Mo(CO)_2L_4$ species was found to be a convenient synthetic route using an "*Öfele*-Birne"[1]. Higher substituted compounds were prepared by the photochemical method[2,4,5].

Table 1. ^{95}Mo *NMR parameters* (*reference: external aqueous 2 M*-Na_2MoO_4 *at pH = 12, all concentrations were approx. 0.4 M, Thf = dried* C_4H_8O *under* N_2)

Compound	δ Mo (ppm)	Solvent
$Mo(CO)_6$	−1 856	*Thf*
$Mo(CO)_5P(C_6H_5)_3$	−1 721 d	*Thf*
$Mo(CO)_5P(OCH_3)_3$	−1 864 d	neat
$Mo(CO)_5P(OC_2H_5)_3$	−1 851 d	neat
$Mo(CO)_4[P(OCH_3)_3]_2$ *cis*	−1 827 t	neat
$Mo(CO)_4[P(OCH_3)_3]_2$ *trans*	−1 845 t	*Thf*
$Mo(CO)_4[P(OC_2H_5)_3]_2$ *cis*	−1 802 t	*Thf*
$Mo(CO)_3[P(OCH_3)_3]_3$ *fac*	−1 756 q	*Thf*
$Mo(CO)_3[P(OCH_3)_3]_3$ *mer*	−1 780 m	*Thf*
$Mo(CO)_3[P(OC_2H_5)_3]_3$ *fac*	−1 721 q	*Thf*
$Mo(CO)_2[P(OCH_3)_3]_4$ *cis*	−1 667 m[a]	*Thf*
$Mo(CO)[P(OCH_3)_3]_5$	−1 556 m[a]	*Thf*

d = doublet, t = triplet, q = quartet, m = multiplet, a = broader lines multiplet.

Table 2. *Spin-spin coupling constants* $^1J(^{95}Mo\text{-}^{31}P)$

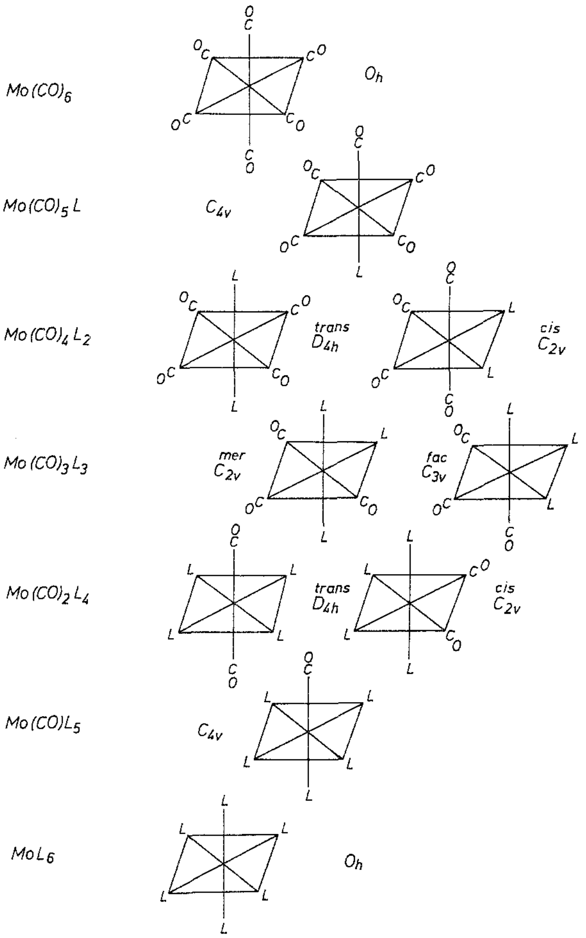
Compounds	Coupling constants obtained from	
	^{95}Mo NMR [Hz]	^{31}P NMR [Hz]
$Mo(CO)_5P(C_6H_5)_3$	135	124 ± 10[6]
$Mo(CO)_5P(OCH_3)_3$	217	216
$Mo(CO)_4[P(OCH_3)_3]_2$ *cis*	217	215
$Mo(CO)_4[P(OCH_3)_3]_2$ *trans*	245	—
$Mo(CO)_3[P(OCH_3)_3]_3$ *fac*	214	213

While this work was in progress two reports appeared of ^{95}Mo-NMR of some molybdenum carbonyls and related compounds showing coincidence with our measurements[3, 8].

A very large range of chemical shifts is found for the nearly complete substituted series of products from δ −1 856 ppm for $Mo(CO)_6$ to δ −1 556 ppm for $Mo(CO)[P(OCH_3)_3]_5$ reflecting the number of $Mo(CO)_6$ carbonyls replaced and their geometry.

Scheme 1 shows the geometrical isomers and their symmetries, Fig. 1 shows the large chemical shift range covered by substituted molybdenum carbonyl species allowing the observation of subtle electronic effects at the molybdenum site.

Scheme 1



Molybdenum-phosphorus spin-spin coupling is detected for phosphine and phosphite substituted species. Table 2 lists the coupling constants obtained either from ^{95}Mo NMR spectra or ^{31}P NMR spectra.

^{31}P NMR chemical shifts and coupling constants (P—P) of some of the prepared compounds are listed in Table 3.

Similar ^{95}Mo chemical shifts of methoxy- and ethoxy-phosphite substituted molybdenum carbonyls [Fig. 1: $L = P(OCH_3)_3$, $L = P(OC_2H_5)_3$] were found reflecting their similar π-acceptor ability and cone angle (107° and 109° respectively). With increasing substitution δ ^{95}Mo is becoming more positive and phosphorous ligands show

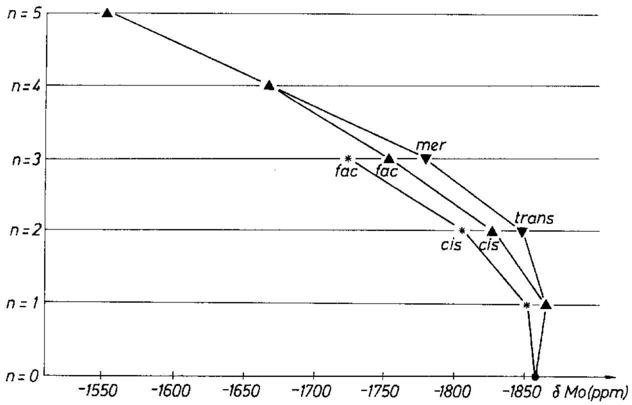


Fig. 1. Chemical shifts for $Mo(CO)_{6-n}L_n$ vs. n [$L = P(OCH_3)_3$ ▲, $L = P(OC_2H_5)_3$ *]

Table 3. ^{31}P *NMR parameters* (*reference:* H_3PO_4, *85%*)

Compounds	δ ^{31}P [ppm]	J (^{31}P-^{31}P)		
		[Hz]	pattern	intensity
$Mo(CO)_3[P(OCH_3)_3]_3$ *mer*	168.3 t 176.3 d	42	d t	2 : 1
$Mo(CO)_2[P(OCH_3)_3]_4$ *cis*	167.9 t 174.7 t	43	t t	1 : 1
$Mo(CO)[P(OCH_3)_3]_5$	163.8 q 174.7 d	47	d q	4 : 1
$Mo[P(OCH_3)_3]_6$	171.9 s			

strong deshielding effects upon the molybdenum nucleus. Further investigations of complete substituted series (e.g. $L = AsR_3$, SbR_3, PX_3 $X = Cl$, Br, I) in order to establish a complete and detailed ^{95}Mo chemical shifts and coupling constants ^1J (^{95}Mo-^{31}P) scale, will elucidate the exact nature of the metal—phosphorous bond with respect to σ- and/or π-interactions between the molybdenum nucleus and the ligand.

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