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CARBONYLNIOBIUM CHEMISTRY

II *. PENTA- AND TETRA-CARBONYLPHOSPHINENIOBATES(—I)

HANS-CHRISTOPH BECHTHOLD and DIETER REHDER *
Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D 2-Hamburg 13 (F.R.G.)

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Summary

The preparation and spectroscopic properties (IR, ^{31}P and ^{93}Nb NMR) of the complexes $[Et_4N][Nb(CO)_5L]$ and *cis*-$[Et_4N][Nb(CO)_4\overline{LL}]$ [$L = PEt_3$, $P(NEt_2)_3$, $P(OMe)_3$; $\overline{LL} = Ph_2P(CH_2)_nPPh_2$ (n = 1—4), $Ph_2As(CH_2)_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$) are described and compared with those of the corresponding vanadium compounds. The complexes $[Et_4N][Nb(CO)_5\overline{LL}]$ (and in some cases *cis*-$[Et_4N][Nb(CO)_4(\overline{LL})_2]$) are identified and characterized spectroscopically. The temperature dependencies of the chemical shifts and half widths of the ^{93}Nb resonances for $[Nb(CO)_6]^-$ are presented.

Introduction

Although the hexacarbonylniobate(—I) has been known for two decades [1,2] and the first derivatives ($[Nb(CO)_5PPh_3]^-$, $[Nb(CO)_4Ph_2P(CH_2)_2PPh_2]^-$, $MNb(CO)_{6-n}L_n$ ($M = Ph_3Sn, Ph_3PAu, EtHg$; $L_n = PPh_3, Ph_2P(CH_2)_2PPh_2$; n = 0—2)) were described more than ten years ago [3,4], no comprehensive study of this group has yet been carried out. We have recently investigated the ^{13}C, ^{19}F, ^{31}P and ^{93}Nb NMR spectroscopic properties of $[Nb(CO)_6]^-$, *fac*-$[Nb(CO)_3(PF_3)_3]^-$ and $[Nb(PF_3)_6]^-$ [5,6], which are of some interest in the light of systematic variations within the vanadium triade. In the present work, we extend this treatment to a larger variety of carbonylphosphineniobates(—I). Some of the trends reported here are in accord with those for phosphine derivatives of η^5-$C_5H_5Nb(CO)_4$ [7].

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* See ref. 7 for communication I.

Results and discussion

Preparation and properties

The complexes $[Et_4N][Nb(CO)_5L]$ $[L = PEt_3, P(NEt_2)_3, P(OMe)_3]$ and *cis*-$[Et_4N][Nb(CO)_4\overline{LL}]$ $[\overline{LL} = Ph_2P(CH_2)_nPPh_2$ (n = 1: dppm, n = 2: dppe, n = 3: dppp, n = 4: dppb), *cis*-$Ph_2PCH{=}CHPPh_2$ (*c*-dpe), $Ph_2As(CH_2)_2PPh_2$ (arphos)] are readily formed by UV irradiation (Duran filter) of THF solutions containing $[Et_4N][Nb(CO)_6]$ and the ligand in approximately equimolar amounts. They form yellow $[P(OMe)_3, P(NEt_2)_3]$ to bright orange (PEt_3), orange-red (dppm, arphos) to dark red (dppe, *c*-dpe) or cerise (dppp, dppb) powders which are extremely (pentacarbonylates) or moderately (chelate complexes) oxygen-sensitive and easily soluble in THF or (*c*-dpe, arphos) THF/CH_3CN. The solutions slowly decompose on standing for several days even at —25° C. The parent carbonyl $[Et_4N][Nb(CO)_6]$ is conveniently prepared by an improved method described by Ellis and Davison [8].

The photoreactions were monitored by IR spectroscopy to optimize the CO replacement with respect to the desired product and to avoid decomposition by too long irradiation times. Optimum reaction times (under standardized conditions) are ca. 80 min for the disubstituted chelate complexes. With the exception of *c*-dpe, the monosubstituted products, formed as intermediates with the bifunctional ligands, can be detected by IR and ^{31}P NMR after 10 to 20 min. The ^{31}P NMR spectra (vide infra) also reveal the formation of disubstituted biligate complexes $[Nb(CO)_4(\overline{LL})_2]^-$ in the case of dppm, arphos and (possibly) dppp and dppb, but not for dppe and *c*-dpe: The formation of the particularly energy-poor chelate 5-rings [6,9] proceeds sufficiently fast to keep back the competing generation of "open" structures.

TABLE 1

IR AND ^{93}Nb NMR DATA

Complex	$\nu(CO)$ [a] (cm^{-1})					$\delta(^{93}Nb)$ [b] (ppm)
$[Nb(CO)_6]^-$	1860					—1672
$[Nb(CO)_5L]^-$						
$L = PPh_3$ [c]	1971s		1863m [d]	1830vs		
$L = PEt_3$	1965m	1897w	1858m [d]	1821vs	1785s	—1595
$L = P(NEt_2)_3$	1966m	1893w	1861s [d]	1817vs	1782sh	—1605
$L = P(OMe)_3$	1977m	1926m	1862s [d]	1834vs	1816sh	—1655
$[Nb(CO)_5\overline{LL}]^-$ [e]	1968m		1861s [d]	1826vs		—1605
cis-$[Nb(CO)_4\overline{LL}]^-$						
$\overline{LL}$ = dppm	1908m	1810vs	1791sh	1745m		—1500
$\overline{LL}$ = dppe [f]	1908s	1806vs	1782sh	1746m		—1490
$\overline{LL}$ = *c*-dpe	1913s	1809vs	1785sh	1747m		—1480
$\overline{LL}$ = arphos	1908s	1802vs	1778s	1746m		—1500
$\overline{LL}$ = dppp	1903s	1791vs	1771vs	1748sh		—1440
$\overline{LL}$ = dppb	1905s	1799vs	1771s	1747m		—1490

[a] In THF or (*c*-dpe and arphos) THF/CH_3CN. [b] Standard: $NbOCl_3$. [c] From ref. 4. [d] This band is probably due to admixtures of $[Nb(CO)_6]^-$ (see text). [e] The data given here ($\overline{LL}$ = dppm) are representative for all monosubstituted complexes of bidentate ligands. [f] Compare ref. 4: 1909, 1803, 1780 and 1750 cm^{-1}.

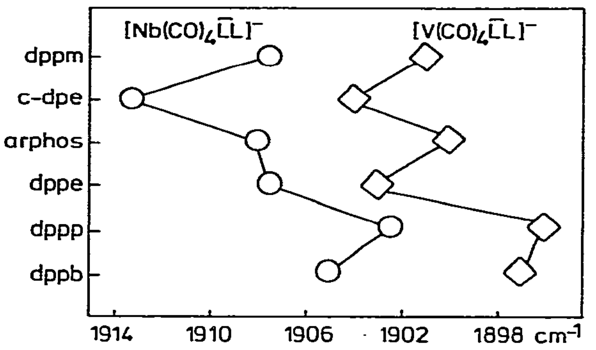

Fig. 1. Variations of the $A_1{}^2$ modes of chelate complexes with the chelate-ring size. See ref. 9 for the data on $[V(CO)_4\overline{LL}]^-$.

IR spectra

The data are collected in Table 1. For $[Nb(CO)_5L]^-$, three bands are expected in the ν(CO) region ($A_1{}^2$, $A_1{}^1$, E). Recent work by Darensbourg [10] suggests that the $A_1{}^1$ and E modes (1820—1830 cm^{-1}) are degenerate accidentally; the CO stretching frequency at ca. 1861 cm^{-1} is then due to unreacted $[Nb(CO)_6]^-$.* If L is a mono-dentate phosphine, a shoulder arises at ca. 1780 ($P(OMe)_3$: 1816) cm^{-1}, possibly indicating the beginning separation of E and $A_1{}^1$. This shoulder may, however, also be due to impurities of $[Nb(CO)_4L_2]^-$. The weak absorption at ca. 1895 ($P(OMe)_3$: 1926) cm^{-1} can be assigned the IR-forbidden B_1, or the $A_1{}^2$ mode of disubstituted complex. Variations in the sharp $A_1{}^2$ mode of the pentacarbonylates (this band is allocated to the four CO groups *cis* to L) are insignificant; this is contrary to the complexes $[V(CO)_5L]^-$ [11] and η^5-$C_5H_5Nb(CO)_3L$ [7].

The complexes *cis*-$[Et_4N][Nb(CO)_4\overline{LL}]$ exhibit four bands ($A_1{}^2$, $A_1{}^1$, B_1, B_2). Except of the $A_1{}^2$ mode, the absorptions are usually broad and partially overlap. As in the η^5-$C_5H_5Nb(CO)_4$ derivatives [7], the chelate 4- and 5-rings show ν(CO) absorptions to higher wave numbers than the 6- and 7-ring structures. The trends also parallel those observed for *cis*-$[V(CO)_4\overline{LL}]^-$ (Fig. 1). The stretching frequencies in the niobium complexes are higher by ca. 7 cm^{-1} than in the vanadium compounds throughout (Fig. 1), which is indicative of the reduced tendency of the Nb centre to delocalize π-electron density into antibonding orbitals of CO.

^{93}Nb NMR spectra

Evaluation of the niobium-93 NMR spectra follows the same pattern as described, e.g., for the nuclei ^{51}V and ^{55}Mn [6]. The quadrupole moment of ^{93}Nb (-0.2×10^{-28} m^2; $I = 9/2$) is four times larger than that of the ^{51}V nucleus, and hence the ^{93}Nb resonances in the C_{4v} and C_{2v} complexes are expected to be

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* This anion shows a single band at 1860 cm^{-1} in THF, contrasting the IR pattern for $[V(CO)_6]^-$ in THF, where an additional weak ν(CO) is observed at 1895 cm^{-1}.

rather broad. For the highly symmetric $[Nb(CO)_6]^-$, where quadrupole broadening should be ineffective, sharp signals arise. At room temperature, the width at half height, $\Delta\nu_{1/2}$, is ca. 10 Hz ($[V(CO)_6]^-$: 1.3 Hz). The line broadens with decreasing temperature, showing that there is no ideal local O_h symmetry and hence a non-vanishing electric nuclear field gradient.

The correlations between temperature, t, the nuclear shielding, $|\delta(^{93}Nb)|$, and $\Delta\nu_{1/2}$, presented graphically in Fig. 2, show the expected trends. The smooth curves indicate that the $\delta(^{93}Nb)/t$ dependence is governed by variations in the occupation of vibronic levels [12,13], while the $\Delta\nu_{1/2}/t$ graph reflects the influence of the molecular correlation time upon the half-width [13,14]. There are no apparent influences arising from dynamic effects originating from exchange equilibria. The temperature gradient, *tg*, of $\delta(^{93}Nb)$ between 203 and 323 K (av. 0.18 ppm/degree) is about half that of $\delta(^{51}V)[V(CO)_6{}^-]$ [15] and ca. one third of the *tg* of $\delta(^{93}Nb)[\eta^5\text{-}C_5H_5Nb(CO)_4]$ [16]. Half widths vary from 9.8 Hz (323 K) to 23.0 Hz (203 K), corresponding to relaxation times T_2 of 32.5 to 13.9 ms.

As in the vanadium complexes, shielding decreases as CO is substituted for the weaker π-accepting phosphine ligands ($[Nb(CO)_6]^- > [Nb(CO)_5L]^- >$

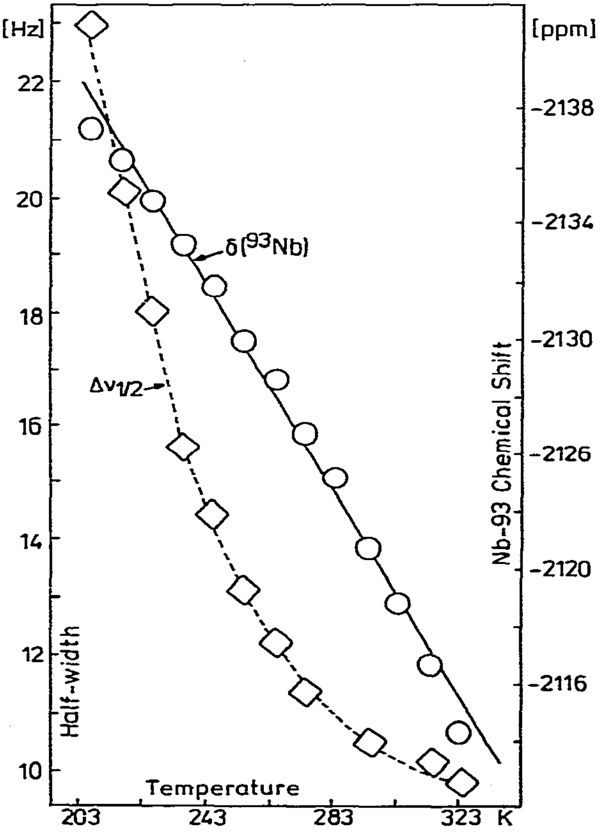

Fig. 2. Nuclear shielding $\delta(^{93}Nb)$ (ref. $NbCl_5$; circles and solid line) and half widths $\Delta\nu_{1/2}$ (squares and broken line) vs. temperature for $[Et_4N][Nb(CO)_6]$ 0.05 *M* THF. Shielding increases from bottom to top.

$[Nb(CO)_4\overset{\frown}{LL}]^-$; cf. Table 1). Within the group of mono-substituted complexes, $|\delta(^{93}Nb)|$ decreases with decreasing π-acceptor ability of the phosphine ($P(OMe)_3 > PEt_3$). The overall changes of $\delta(^{93}Nb)$ (−1672 to −1460) are less significant than those of $\delta(^{51}V)$ (−1952 to −1590 ppm [15]); and while there are rather large variations of $\delta(^{51}V)$ with the chelate-ring size [9], the $\delta(^{93}Nb)$ values are practically the same for all $[Nb(CO)_4\overset{\frown}{LL}]^-$. This observation might again reflect the diminished π-delocalizing capability of Nb: We have shown earlier [6,11,15] that, in many cases, the π-interaction between the metal centre and the ligand periphery is the main factor influencing variations in the overall shielding of the metal nucleus, an effect which should be less pronounced in the niobium complexes.

^{31}P NMR spectra

In contrast to the anionic vanadium complexes, the niobium species exhibit rather sharp ^{31}P resonances for the coordinated phosphorus functions. This is due to an almost complete decoupling of the ^{31}P and ^{93}Nb nuclei at sufficiently low temperatures (<250 K) and agrees well with the expected greater quadrupole interaction (higher relaxation rates) for the ^{31}P nucleus ligated to ^{93}Nb.

The well resolved ^{31}P NMR spectra (for data collection see Table 2) allow for

TABLE 2

^{31}P NMR DATA

Complex	$\delta(^{31}P)$ [a] (ppm)			$\Delta\delta_P$ [b]	ΔR [c]
	free ligand	uncoord. PPh_2	coord. PPh_2		
$[Nb(CO)_5L]^-$					
$L = PEt_3$	−20.4	—	+19	39	—
$L = P(NEt_2)_3$	+115.5	—	+159	43	—
$L = P(OMe)_3$	+139.6	—	+185	45	—
$[Nb(CO)_5\overset{\frown}{LL}]^-$					
$\overset{\frown}{LL}$ = dppm	−25.3	−24.8(d) [d]	+30.1(d) [d]	55.4	—
$\overset{\frown}{LL}$ = dppe	−15.3	−14.0(d) [e]	+35.2 [f]	50.5	—
$\overset{\frown}{LL}$ = arphos	−14.9	—	+35.6	50.5	—
$\overset{\frown}{LL}$ = dppp	−19.6	−21.0	+30.2	49.8	—
$\overset{\frown}{LL}$ = dppb	−17.8	−17.4	+31.0	48.8	—
$[Nb(CO)_4(\overset{\frown}{LL})_2]^-$					
$\overset{\frown}{LL}$ = dppm		−27.6(d) [g]	+26.3(d) [g]	51.6	—
$\overset{\frown}{LL}$ = arphos		—	+27.0	41.9	—
$\overset{\frown}{LL}$ = dppp [h]			+28.4	48.0	—
$\overset{\frown}{LL}$ = dppb [h]			+28.4	46.2	—
$[Nb(CO)_4\overset{\frown}{LL}]^-$					
$\overset{\frown}{LL}$ = dppm		—	+8.4	33.7	−17.9
$\overset{\frown}{LL}$ = dppe		—	+53.4	68.7	+17.1
$\overset{\frown}{LL}$ = *c*-dpe		—	+62.0 [i]	86.2	+34.6
$\overset{\frown}{LL}$ = arphos		—	+57.2	72.1	+20.5
$\overset{\frown}{LL}$ = dppp		—	+24.0	44.0	−7.6
$\overset{\frown}{LL}$ = dppb		—	+31.4	49.5	−2.1

[a] In THF solution at 205 K. [b] ^{31}P coordination shift (see text). [c] Chelate-ring contribution to $\Delta\delta_P$ (see text and ref. 17). [d] $^2J(PP)$ 100 Hz. [e] $^3J(PP)$ 30 Hz. [f] Partially resolved only. [g] $^2J(PP)$ 55 Hz. [h] Tentative assignments. [i] An additional sharp signal at −9.0 ppm is not assigned.

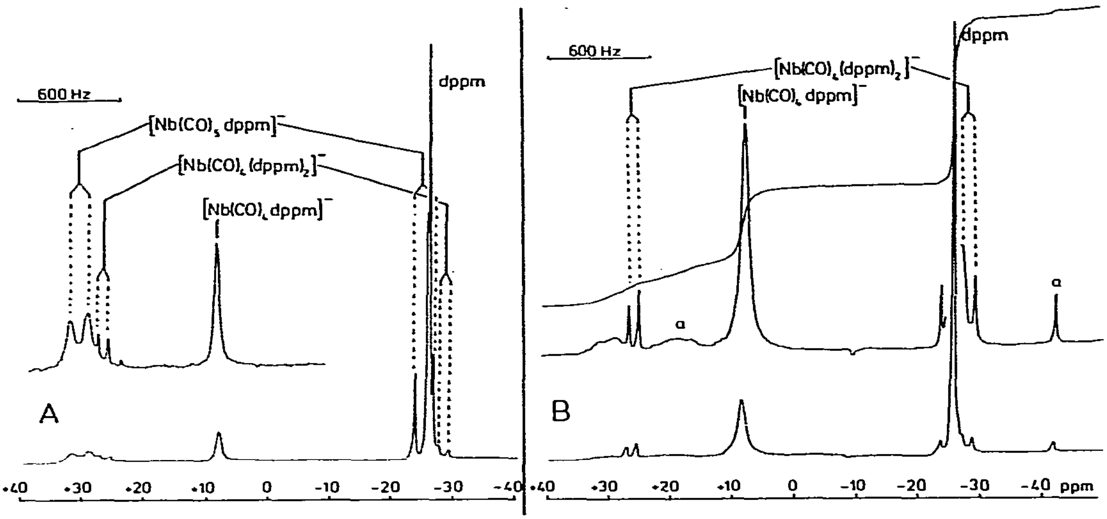

Fig. 3. 36.44 MHz $^{31}P\{^1H\}$ NMR spectra of the reaction products produced during irradiation of $[Et_4N]$-$[Nb(CO)_6]$ and $Ph_2PCH_2PPh_2$ in THF (a: unassigned). Irradiation times: 20 min (A) and 80 min (B).

the evaluation of the reaction path as demonstrated for the reaction products formed between $[Nb(CO)_6]^-$ and dppm after 20 min and 80 min irradiation, respectively (Fig. 3).

The mono-substituted complexes $[Nb(CO)_5\overline{LL}]^-$, which are formed as the first intermediate, are characterized by a very sharp doublet (uncoordinated PPh_2) close to the signal corresponding to the free ligand, and a broader doublet (coordinated PPh_2) typically shifted to low field. Further irradiation proceeds with the formation of the disubstituted complexes *cis*-$[Nb(CO)_4\overline{LL}]^-$ (singlet) and, in the case of dppm, arphos and (presumably) dppp and dppb, *cis*-$[Nb(CO)_4(\overline{LL})_2]$ (two doublets).

All coordination shifts $\Delta\delta_P = \delta(^{31}P)$ [coordinated ligand] $- \delta(^{31}P)$ [free ligand] are positive. Ring contributions $\Delta R = \Delta\delta_P[Nb(CO)_4(\overline{LL})_2^-] - \Delta\delta_P$ [chelate complex] (for a comprehensive treatment of ΔR see [17]; here, we employ $\Delta\delta_P$ for $[Nb(CO)_4(dppm)_2]^-$ as a reference) are largest for the unstrained chelate 5-rings; they are negative for dppm, dppp and dppb with the strained 4-ring exhibiting the largest negative value. These findings are in accord with those on η^5-$C_5H_5M(CO)_2\overline{LL}$ (M = Nb [7], M = V [9]), $HV(CO)_4\overline{LL}$ [9] and other transition metal diphosphine complexes [9,17].

Experimental

General

All operations were carried out under nitrogen and in dry solvents. The irradiation apparatus described in ref. 7 was employed in all reactions.

Phosphines were obtained from commercial sources (Strem), and $[Nb(CO)_6]^-$ was prepared by the method of Ellis and Davison [8], and isolated from the filtered diglyme solution as the tetraethylammonium salt (addition of 19.1 g

$[Et_4N]Cl$ dissolved in 115 ml EtOH, followed by treatment with 900 ml H_2O); $[AsPh_4][Nb(CO)_6]$ (which is the isolated form in Ellis' description) is light-sensitive. To improve the yield, the contents of the autoclave were extracted several times with light petrol ether.

Spectroscopic measurements were carried out as described in ref. 7. ^{93}Nb NMR spectra ($[Nb(CO)_6]^-$: Bruker WH 90, other: Varian DP 60) were recorded relative to $NbCl_5/CH_3CN$ and are quoted relative to $NbOCl_3$ ($\delta(NbOCl_3) = 0$, $\delta(NbCl_5) = +460$ ppm). Absolute errors: ±0.3 ($[Nb(CO)_6]^-$), ±5 ($[Nb(CO)_5L]^-$), ±20 ($[Nb(CO)_4\overline{LL}]^-$).

Preparation of phosphine complexes

Preparative details are given in Table 3. About equimolar amounts (ca. 10% excess of the ligand is necessary for a complete conversion to $[Nb(CO)_4\overline{LL}]^-$) of $[Et_4N][Nb(CO)_6]$ and the phosphine were dissolved in 20 to 30 ml THF and irradiated, until the IR spectrum (CO region) showed a constant pattern. During this time, the solution changed from yellow to deep-red. The complexes $[Et_4N][Nb(CO)_4c\text{-dpe}]$ and $[Et_4N][Nb(CO)_4\text{arphos}]$ begin to precipitate in the course of the reaction or shortly afterwards. $[Et_4N][Nb(CO)_4\text{dppp}]$ crystallizes from the concentrated solution, and $[Et_4N][Nb(CO)_4\text{dppm}]$ from a solution concentrated to 1 ml layered with n-heptane, during standing at —25°C for ca. 1 day. The other complexes are precipitated by stirring the concentrated solutions with heptane (8 ml per 1 ml THF). $[Et_4N][Nb(CO)_5PEt_3]$ and $[Et_4N][Nb(CO)_5P(NEt_2)_3]$ immediately form micro-crystalline powders upon this treatment, while sticky products are obtained in the case of $[Et_4N][Nb(CO)_4\text{dppe}]$ and $[Et_4N][Nb(CO)_4\text{dppb}]$. These complexes solidify when stirred vigorously for 2 days. $[Et_4N][Nb(CO)_5P(OMe)_3]$ (probably containing some $[Et_4N][Nb(CO)_4\{P(OMe)_3\}_2]$) was isolated as a viscous oil, which only partly crystallized. The complexes were filtered off, washed twice with 5 ml portions of THF/heptane 1/8, and dried under high vacuum (0.01 Torr, 5 h).

TABLE 3

PREPARATIVE DETAILS

Complex	Weighed samples				Irradiation time (min) [a]	Yield (%)
	$[Et_4N][Nb(CO)_6]$ (mg)	(mmol)	Phosphine (mg)	(mmol)		
$[Et_4N][Nb(CO)_5PEt_3]$	390	1.0	120	1.0	45	73
$[Et_4N][Nb(CO)_5P(NEt_2)_3]$	390	1.0	290	1.2	50	75
$[Et_4N][Nb(CO)_5P(OMe)_3]$	420	1.1	150	1.2	40	60
$[Et_4N][Nb(CO)_4\text{dppm}]$	310	0.8	390	1.0	80	40
$[Et_4N][Nb(CO)_4\text{dppe}]$	195	0.5	450	1.1	75	72
$[Et_4N][Nb(CO)_4c\text{-dpe}]$	310	0.8	400	1.0	70	75
$[Et_4N][Nb(CO)_4\text{arphos}]$	350	0.9	450	1.0	70	71
$[Et_4N][Nb(CO)_4\text{dppp}]$	240	0.6	310	0.75	80	63
$[Et_4N][Nb(CO)_4\text{dppb}]$	280	0.7	325	0.75	80	58

[a] Irradiation times for optimum yields of monosubstitution product with bidentate ligands are 8 min (dppe, *c*-dpe, arphos, dppp) and 23 min (dppm, dppb), respectively.

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