Journal of Organometallic Chemistry, 310 (1986) 107–114
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CLEAVAGE AND REARRANGEMENT OF PHOSPHORUS–CARBON AND PHOSPHINE–METAL BONDS IN ALKYLTRIS(TERTIARY PHOSPHINE)COBALT COMPOUNDS

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(Received January 15th, 1986)

Summary

Complexes of the type L_3CoCH_3 have been prepared in which $L = Ph_3P$, P_2PCH_3, $PhP(CH_3)_2$, $Ph_2PGe(CH_3)_3$, $Ph_2PSn(CH_3)_3$, Ph_3As, and $R = CH_3$, Ph, and $(CH_3)_3Si$. Decomposition of these complexes under mild conditions in several solvents has been studied. Among the identified products are benzene, toluene, biphenyl, and rearranged phosphines, such as Ph_3P from $[Ph_2PCH_3]_3CoCH_3$ or Ph_2PCH_3 from $[Ph_2PGe(CH_3)_3]_3CoCH_3$.

Extensive decomposition of triphenylphosphine ligands in the compound $[Ph_3P]_3CoCH_3$ has been reported previously [1]. Products of this reaction include biphenyl, benzene, toluene and methyldiphenylphosphine. The reactions of similar compounds $[Ar_3P]_3CoCH_3$ in which Ar = 3- and $4\text{-}CH_3C_6H_4$, yield biaryls which are the products of coupling at the specific carbon which was previously bonded to phosphorus. Carbon–phosphorus bonds are thus cleaved, with consequent reductive coupling of aryl residues with each other or with the cobalt-bonded methyl group, or else with a hydrogen atom from an unspecified source. Formation of methyldiphenylphosphine, on the other hand, reflects a more complicated transformation of the phosphine in which phosphorus-bonded phenyl groups are replaced by cobalt-bonded methyl groups in a manner not previously described [2].

Triphenylphosphine is regarded as a relatively unreactive ligand, and catalysts based on its compounds with transition metals are very often used. However, decomposition of this ligand has been described in several cases, as, for example, even more than ten years ago when $IrH(CO)(Ph_3P)_2$ was transformed to $Ir_2(\mu_2\text{-}PPh_2)_2(CO)_2(PPh_3)_2$ [3]. The reaction of $Os_3(CO)_{12}$ with Ph_3P [4] as well as the thermal decomposition of $(Ph_3P)_4Pt$ [5] yielded clusters containing $\mu_2\text{-}Ph_2P$ bridges

0022-328X/86/$03.50

between metal atoms and phenyl residues bonded to Os and Pt respectively. The reaction of $[Ph_3P]Ni[Et_3P]_2$ [6] yielded dimers containing μ_2-Ph_2P bridges and biphenyl. Similar formation of biphenyl from Ph_3P ligands at elevated temperatures was also observed with palladium [7], platinum [8], and rhodium [9] complexes. Such cleavages are not limited to arylphosphines. A case in which a butyl residue is cleaved off a tributylphosphine complex was recently described [10]. Another report described the formation of ethane, ethane-d_3 and ethane-d_6 from $Pd(CH_3)_2(Ph_2PCD_3)_2$ [11]. Examples of decomposition of the triphenylphosphine ligand during a catalytic reaction have been reported with increasing frequency, and the significance of such reactions for the performance of the catalysts was recognised recently [12,13].

$[Ph_3P]_3CoCH_3$ has been described as exceptional in that ligand decomposition occurred at temperatures as low as 0°C [1,2]. Indications that in addition to cleavage and coupling, rearrangement of the ligand occurred prompted us to study additional members of the series L_3CoR. The experiments described below concern the reactivity of the phosphine ligand, and it now seems that these reactions may be more complex than previously thought.

Results and discussion

Compounds of the type L_3CoCH_3 (I) were prepared by interaction of $Co(acac)_3$, $(CH_3)_3Al$ and a tertiary phosphine ligand L.

$$Co(acac)_3 + (CH_3)_3Al + R_2PR' \rightarrow (R_2PR')_3CoCH_3$$

The following compounds were prepared by this method: Compounds $(R_2PR')_3CoCH_3$ I-1: $R = R' = C_6H_5$; I-2: $R = C_6H_5$, $R' = CH_3$; I-3: $R = CH_3$, $R' = C_6H_5$; I-4: $R = C_6H_5$, $R' = Ge(CH_3)_3$; I-5: $R = C_6H_5$, $R' = Sn(CH_3)_3$).

The compound $(Ph_3As)_3CoCH_3$ (I-6) was similarly made from triphenylarsine. A trimethylsilylcobalt derivative was prepared by the following reaction:

$$2Co(acac)_3 + Al[Si(CH_3)_3]_3 + 6Ph_3P \rightarrow \underset{\text{(I-8)}}{2(Ph_3P)_3CoSi(CH_3)_3}$$

The aluminium compound [14] can be replaced in these reactions by $[(CH_3)_3Si]_2Hg$ [15] or $[(CH_3)_3Si]_2Mg$ [16].

Alkylation of anhydrous cobaltous chloride was used to prepare the corresponding phenyl derivative:

$$PhLi + CoCl_2 + 3Ph_2PCH_3 \rightarrow \underset{\text{(I-7)}}{(Ph_2PCH_3)_3CoPh}$$

This method was also used to prepare compounds (I-1)–(I-3) but there were difficulties in removing residual $CoCl_2$. Use of $Co(acac)_3$ will under certain circumstances, depending on the structures of the ligands, yield compounds of the type $L_2Co(acac)(CH_3)_2$ and $L_3Co(CH_3)_3$ [17]. None of the compounds listed in Table 1 appear to have such structures (analysis) or give any indication of the presence of acetylacetonate (IR, NMR).

The IR spectral data for the compounds listed in Table 1 consistently show bands at 439–462 cm^{-1} attributed to ν(CO–C) in $CoCH_3$, while complex I-8 shows a band at 250 cm^{-1} attributed to ν(CO–Si); by comparison, $SiH_3Co(CO)_4$ shows a

TABLE 1

IR- AND NMR-FREQUENCIES FOR L_3CoR DERIVATIVES

Compound	ν(Co–C) (cm^{-1})	ν(Co–P) (cm^{-1})	$\delta(CH_3Co)$ [a] (ppm)	$\delta(CH_3M)$ [b] (ppm)	$\delta(^{31}P)$ [e] (ppm)
I-1 [2]	462	295	−0.4	–	+25.80
I-2	445	368	−0.04	1.94 [b]	+30.58
I-3	439	320	−0.30	1.46 [b]	+41.20
I-4	450	255	−0.30	0.16 [c]	+29.65
I-5	455	376	+0.08	1.95 [d]	+22.53
I-6	451	–	+0.41	–	–
I-8	Co–Si 250	301	–	–	+16.95

[a] At 298 K. In the ^{1}H NMR spectrum the $CoCH_3$ protons give one or two partially resolved multiplets, the shifts of which changes as decomposition occurs; [b] M = P. [c] M = Ge. [d] M = Sn. [e] Shifts for the free ligands are: Ph_3P −6; Ph_2PCH_3 −28; $PhP(CH_3)_2$ −46 ppm [20].

band at 306 and $CH_3SiCo(CO)_4$ at 295 cm^{-1} [18]. Bands observed in the range of 295–376 cm^{-1} may be related to ν(C–P) as they are absent from the spectrum of I-6; this is also supported by analogy [19]. Sharp signals are obtained in the ^{1}H and ^{31}P NMR spectra, and the compounds are clearly diamagnetic, but there was occasionally loss of fine resolution due to paramagnetic residues. In the ^{1}H NMR spectra the $CoCH_3$ groups show multiplets between 0.0 and −3.4 ppm (TMS). ^{31}P resonances for the phosphine complexes are between +16.9 and +42 ppm (H_3PO_4 25%). As with I-1 [2], dissociation of phosphine from I-2 is apparent from the spectrum, which shows peaks at +30.58, +25.2, and −27.3 (dissociated Ph_2PCH_3) [20] when this compound is kept in toluene-d_8 or benzene-d_6 for 1 h at room temperature. Compounds I-4 and I-5 show no evidence of such dissociation. Instead, after several hours in solution several phosphorus resonances appear, implying decomposition. None of these peaks can be assigned to the free ligand.

All these compounds are soluble in THF and aromatic solvents, insoluble in pentane and slightly soluble in diethyl ether. They were isolated as powders, and as such are stable under Ar atmosphere at room temperature for many months. They decompose on exposure to water and to oxygen and may be pyrophoric e.g. I-3.

A solution of ~ 10^{-4} mole of the complex in 10 ml of solvent was examined at the specified temperature and time (Table 2). Work-up involved acid hydrolysis followed by separation of the organic and inorganic material and analysis of the complete organic phase. Decomposition products from various cobalt complexes are listed in Table 2, and reflect both cleavage of phenyl groups from phosphines and rearrangement of phosphine ligands.

Products such as benzene and toluene from compounds I-1 to I-3 as well as I-6 in THF were determined along with biphenyl by HPLC, but were too volatile to be properly estimated along with phosphines by GC or GC-MS. By comparison with biphenyl they were present in very small amounts. Quantitative isolation of phosphines from the product mixture was impossible, and the ratios of products within the phosphine fraction provide a more accurate picture than actual yields.

Formation of biphenyl from compounds with Ph_2PCH_3 ligands was considerable. Biphenyl was also formed from the triphenylarsine compound. Only a trace was obtained from complexes of $PhP(CH_3)_2$, and none from the germyl and stannyl compounds I-4 and I-5.

TABLE 2

DECOMPOSITION OF L_3COR IN SOLUTIONS

L	R	Solvent	Time (h)	Temperature (°C)	Products (ratio)[b]					Remarks[a]
Ph_2PCH_3 (I-2)	CH_3	THF	24	20	PhPh (2):	Ph_2PCH_3 (20)	$Ph_2(PO)CH_3$ (8)	Ph_3P (1)	Ph_3PO (–)	
Ph_2PCH_3 (I-2)	CH_3	THF	1	60	PhPh (3);	Ph_2PCH_3 (18)	$Ph_2(PO)CH_3$ (4)	Ph_3P (6)		
Ph_2PCH_3 (I-2)	CH_3	4-chloro-toluene	24	20	–	Ph_2PCH_3 (30)	$Ph_2(PO)CH_3$ (10)	Ph_3P (1)		
			24	100	PhPh (1)	Ph_2PCH_3 (16.4)		Ph_3P (4.7)		
Ph_2PCH_3 (I-7)	Ph	THF	0.5	50	PhPh (3)	Ph_2PCH_3 (20)	$Ph_2(PO)CH_3$ (8)	Ph_3P (2)	Ph_3PO (2)	
Ph_2PCH_3 (I-7)	Ph	4-chlorotoluene	24	20	PhPh (1)	Ph_2PCH_3 (2)	$Ph_2(PO)CH_3$	Ph_3P (0.16)		
			24	100	PhPh (1)	Ph_2PCH_3 (2)		Ph_3P (1)		
Ph_2PCH_3 (I-7)	Ph	2-bromo-naphthalene	0.5	50	PhPh (1)		$Ph_2(PO)CH_3$ (15)			(x)
$PhP(CH_3)_2$ (I-3)	CH_3	THF	1	50	trace	$PhP(CH_3)_2$ (10)	$Ph(PO)(CH_3)_2$ (2)	Ph_2PCH_3 (1)		
Ph_3As (I-6)	CH_3	THF	24	20	trace (1)				Ph_3As (10)	
$Ph_2PGe(CH_3)_3$ (I-4)	CH_3	THF	24	20		$PhP(CH_3)_2$ (1)			Ph_3PO (1)	(x)
$Ph_2PGe(CH_3)_3$ (I-4)	CH_3	*p*-chloro-toluene	24	20	PhPh (1)	$Ph_2(PO)CH_3$ (20)			Ph_3PO (6)	(x)
$Ph_2PSn(CH_3)_3$ (I-5)	CH_3	THF	24	20		$Ph_2(PO)CH_3$				(x)
$Ph_2PSn(CH_3)_3$ (I-5)	CH_3	2-bromo-naphthalene	24	20						(x)
Ph_3P (I-8)	$Si(CH_3)_3$	THF	24	20					Ph_3P	(x)
Ph_3P (I-8)	$Si(CH_3)_3$	2-methyl-naphthalene	0.5	80	PhPh (3)	$PhSi(CH_3)_3$ (trace)			Ph_3P (40)	(x)
Ph_3P (I-8)	$Si(CH_3)_3$	THF	1	50	PhPh (3)	$PhSi(CH_3)_3$ (2)			Ph_3P (40)	(x)
Ph_3P (I-8)	$Si(CH_3)_3$	2-bromo-naphthalene	0.5	80	$2\text{-}C_{10}H_7Si(CH_3)_3$ (1)				Ph_3P (15)	(x)

[a] (x) Accompanied by several unidentified products. [b] Ratios are based on analyses by GC on Silicone SE 30 with TC detector and confirmed by analysis by GC-MS with EI and CI ionization which showed essentially the same picture.

The trimethylsilyl derivative I-8 yielded trimethylsilylbenzene, but the decomposition required higher temperatures (2-methylnaphthalene as solvent at 80°C), there was also very little decomposition to biphenyl. This derivative I-8 seems to be less reactive than its methyl counterpart I-1. However, with solvents like 4-chlorotoluene or 2-bromonaphthalene only I-8 and I-1 yielded products of oxidative addition [1,2] like 2-trimethylsilylnaphthalene bonds from 2-bromonaphthalene and I-8. In view of the inherent stability of transition-metal–silyl bonds compared with metal–alkyl bonds (due to metal to silicon d–π bonding [21]), this result was somewhat surprising.

More notable was the rearrangement of phosphines. Formation of Ph_3P from I-2 and I-7 is evidently cobalt catalysed. Comparison of reactions at 20°C and at 50, 60 or 100°C in THF or chlorotoluene show significant increase of the proportion of Ph_3P in product mixtures from I-2 and I-7. With I-3 there is evidence for transformation $PhP(CH_3)_2$ to Ph_2PCH_3. Rearrangement is even more obvious with I-4, where it involves cleavage of the more sensitive P–Ge link, yielding Ph_2PCH_3 and Ph_3P. The high reactivity of the Ge–P bond is well documented [22], yet free $Ph_2PGe(CH_3)_3$ remains intact under similar conditions even in the presence of $CoCl_2$. The stannyl complex I-5 yielded Ph_2PCH_3 but not Ph_3P. In the case of I-4 and I-5 other, unidentified, phosphorus-containing products were present, and the picture is far from being completely resolved. An interesting analogy to this regrouping around phosphorus with cleavage of the weakest available C–P bond, i.e. the selective cleavage of an alkyne–phosphorus bond, has been described by Carty et al. [23]:

$$Fe_3(CO)_{11}(Ph_2PC{\equiv}CR) \rightarrow Fe_2(C{\equiv}CR)(CO)_6(PPh_2) + (CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)Fe(CO)_3$$

A redistribution reaction of triarylphosphines at elevated temperatures catalysed by a rhodium compound was recently reported [24] (Tol = $4\text{-}CH_3C_6H_4$–):

$$Ph_3P + Tol_3P \xrightarrow[130\,°C]{\text{Rh cat.}} Ph_2TolP + PhTol_2P$$

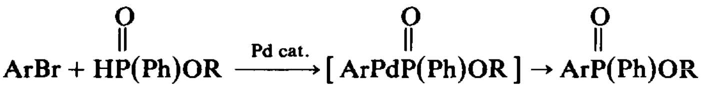
Another recent report [25] describes the analogous disproportionation of amines, such as:

$$Et_3N + Pr_3N \xrightarrow[125\,°C]{\text{Ru cat.}} Et_2NPr + Pr_2NEt$$

In our case scrambling was detected only for phosphines bonded in a complex and not for the free phosphines.

Both cleavage and rearrangement were found to interfere with catalytic reactions. Carbonylation with $RhH(CO)(Ph_3P)_3$ at 130°C under 80 psi of H_2 and CO, yielded products such as C_6H_5CHO, and when propene is the substrate it is incorporated into the phosphine structure to give the compound $RhH(CO)_2(Ph_3P)(Ph_2PC_3H_7)$. Conversion of non-bonded Ph_3P to $Ph_2PC_3H_7$ under hydrogenation conditions with $RhH(CO)(Ph_3P)_3$ was also demonstrated [24]. Fahey and Mahan reported formation of $PhCH{=}CHCO_2Et$ from $CH_2{=}CHCO_2Et$, $Pd(OAc)_2$ and Ph_3P as long ago as 1976 [6].

An interesting rearrangement in the opposite direction has been suggested for the addition of ArBr to Pd^0 which involves the shift of an aryl group from the metal to phosphorus [26]:



$$\mathrm{ArBr} + \mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{Ph})\mathrm{OR} \xrightarrow{\text{Pd cat.}} [\,\mathrm{ArPd}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{Ph})\mathrm{OR}\,] \rightarrow \mathrm{Ar}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{Ph})\mathrm{OR}$$

Reports of such ligand behaviour are still scarce, but may now be expected with increasing frequency. The great majority of reports on homogeneous catalysis make no mention of it, and it probably does not occur very often. In some reported cases the possibility of such reactions should perhaps be considered; e.g. the formation of benzene and diphenylphosphine during hydrogenation with a Ph_3P catalyst [27]. The increasing number of observations of phosphine decomposition implies that this may affect the reactivity and lifetime of the catalyst.

Very little can yet be said about the mechanism. Previous results available were rationalized by suggesting oxidative addition to the C–P bond [6,1,2], and this has recently been proposed again, but with no additional evidence [28], for the more complex interference with the reactions of phosphinerhodium catalysts. It seems to us that explanations advanced so far are insufficient for the more complicated rearrangements involving several migrations of substituents around phosphorus.

Experimental

Cobalt compounds were prepared under an Ar atmosphere in dry solvents. The phosphines $Ph_2PGe(CH_3)_3$ and $Ph_2PSn(CH_3)_3$ have been described previously [29,30]. Spectra were recorded on Perkin–Elmer 327, 580-B, Bruker WP 80 and WH 300 instruments. HPLC Lichrosorb column with 3/1 acetonitrile/water was used for separations of benzene, toluene and biphenyl. A Varian Mat 44 (with 70 eV EI or CI with methane or isobutane) was used for GC-MS. Phosphines were analysed in mixtures with their corresponding oxides.

Preparation of compounds L_3CoCH_3. To a mixture of cobalt acetylacetonate (1.1 g, 3 mmol) mixed with the relevant phosphine or arsine (9 mmol) in 70 ml diethyl ether at −35 °C, a solution of trimethylaluminum (0.34 g, 4.75 mmol) in 15 ml pentane was added with stirring. After 2 h the temperature was raised to 0 °C, and a brown precipitate formed. Some of the solvent was evaporated off and 30 ml pentane were added. The precipitate was filtered off, washed with pentane at −30 °C, and dried under vacuum at room temperature.

Methyltris(diphenylmethylphosphine)cobalt. Yield: 1.38 g (68%) orange powder, m.p.(dec.) 88 °C. Found: C, 70.51; H, 7.11. $C_{40}H_{42}CoP_3$ calcd.: C, 71.21; H, 6.28%.

Methyltris(phenyldimethylphosphine)cobalt. Yield: 0.84 g (57%) brown powder, m.p.(dec.) 50–52 °C. Found: C, 60.15; H, 7.65. $C_{25}H_{36}CoP_3$ calcd.: C, 61.48; H, 7.43%.

Methyltris(triphenylarsine)cobalt. Brown powder, m.p. (dec) 60 °C. Found: C, 65.2; H, 5.1. $C_{55}H_{48}As_3Co$ calcd.: C, 66.9; H, 4.83%.

Methyltris(diphenyltrimethylgermylphosphine)cobalt. Yield 1.62 g (55%) brown powder, m.p.(dec) 96 °C. Found: C, 56.02; H, 5.49. $C_{46}H_{60}CoGe_3P_3$ calcd.: C, 56.23; H, 6.15%.

Methyltris(diphenyltrimethylstannylphosphine)cobalt. Yield 1.48 g (44%) light brown powder, m.p. (dec.) 75°C. Found: C, 50.2; H, 5.24. $C_{46}H_{60}CoP_3Sn_3$ calcd.: C, 49.29; H, 5.40%.

Trimethylsilyltris(triphenylphosphine)cobalt. A mixture of $Co(acac)_3$ 1.1 g (3 mmol) and triphenylphosphine 2.35 g (9 mmol) in 65 ml pentane/THF 3/1 was at −25°C as tris(trimethylsilyl)aluminum · (Et_2O) 4.33 g (13.5 mmol) in 20 ml pentane was added. The colour changed from green to brown during 3 h of stirring. The temperature was then raised to 0°C and some of the solvent was evaporated off. The solution was kept at −30°C, and the solid which separated was filtered off in vacuum to yield 1.1 g (40%) of a pink powder, m.p.(dec.) 42°C. Found: C, 71.44; H, 5.05. $C_{57}H_{54}CoP_3Si$ calcd.: C, 74.49; H, 5.92%.

Phenyltris(diphenylmethylphosphine)cobalt. A mixture of methyldiphenylphosphine (1.8 g, 9 mmol) and PhLi (1.2 mmol) in 70 ml THF was treated at 0°C with anhydrous $CoCl_2$ (3 mmol), (dried at 120°C for 1 h), then filtered cold. The solvent was evaporated off from the clear filtrate until the volume was reduced to one-third, then cold pentane was added. The solid was filtered off and repeatedly washed with pentane to yield a brown powder m.p.(dec.) 65°C. Found: C, 70.5; H, 5.8. $C_{45}H_{44}CoP_3$ calcd.: C, 73.4; H, 6.0%.

$Ph_2PGe(CH_3)_3$ control test A. This compound has a well resolved ^1H NMR spectrum (ppm): CH_3, 0.34 (doublet, J 0.02 Hz), Ph, 7.11 and 7.50 (multiplet) and gives a ^{31}P resonance at −50 ppm (singlet). Both spectra remained unchanged when a solution in 4-chlorotoluene was kept at room temperature at 70°C for 48 h, with and without the addition of $CoCl_2$. In contrast the spectra of complex I-4 showed changes after 0.5 h in this solvent or in THF at room temperature. The ^{31}P spectrum shows several bands, none for the original ligand.

$Ph_2PGe(CH_3)_3$ control test B. The behaviour of this compound was examined by GC-MS under the same conditions as for I-4 with the inlet temperature set at 100 and 200°C respectively, and the GC column at 100°C. Ionization was by EI 70 eV. The mass spectrum showed molecular ions with the pattern expected for a germanium containing species, m/e (intensity) at 300 (20.5) and 302 (27.5), 303 (7.8), 304 (36), 305 (8) and 306, ions from a second such species at 284, 286, 287, 288, 289 and 290, with the same intensity distribution, ions at 272 and 273, overlapping clusters of ions at 231 and 233. The base peaks were at 184 and 186, as is typical when Ph_2P groups are present. Relative intensities in the complete spectrum: 304 (65); 284 (7); 231 (24); 184 (100). There was no trace of ions at m/e 278 and 262 (Ph_3PO and Ph_3P) or 216 and 200 ($Ph_2P[O]CH_3$ and Ph_2PCH_3).

Control test for Ph_2PCH_3. Analysis by GC-MS of this phosphine was carried out with the source initially at ambient temperature, then at 100, 160 and 190°C. The spectrum at ambient temperature showed peaks at m/e 200 (100), 199 (54), 185 (26), 184 (55), 183 (82), 182 (27), 152 (14), 121 (14), 120 (13), 107 (15), 106 (12), 100 (10), 91 (18), 90 (10), 78 (12), 77 (23), 65 (10) and 51 (24); At higher inlet temperature the ion of m/e 183 became the base peak, along with 200 (92) and changes in the abundance of a few other ions. The ion at m/e 262 (3) was detected only when the inlet system was set at 190°C. The complexes were examined with the inlet set at 100°C.

Other complexes tested. The compounds $(Ph_3P)_3CoCl$ and $(Ph_2PCH_3)_3CoCl$ showed no evidence of decomposition of the phosphine ligands.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support and the TU Berlin for special grants in connection with partnership agreements between the TU Berlin and the HU Jerusalem. We also thank Prof H. Schwarz and Dr. G. Hoehne of the TU for their help with the GC-MS analyses.

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