Main Group Met. Chem. 2015; 38(5-6): 169–173

Short Communication

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$[4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2Sn(PPh_3)Cr(CO)_5}]\mathrm{ClO_4}$ – a salt containing a cationic triphenylphosphane-stabilized organostannylene transition metal complex

DOI 10.1515/mgmc-2015-0028
Received September 1, 2015; accepted September 9, 2015; previously published online October 13, 2015

Abstract: The isolation and molecular structure of bis(di-*iso*-propoxyphosphonyl)-4-*tert*-butyl]phenyl}tin triphenylphosphane perchlorate chromium pentacarbonyl, **2**, is reported. It is the first example of an ionic compound containing an organostannylene transition metal complex cation stabilized by a phosphane donor. Slow reaction of compound **2** in acetonitrile gave *trans*-bis-triphenylphosphane chromium tetracarbonyl, *trans*-$(Ph_3P)_2Cr(CO)_4$, in a new crystalline modification.

Keywords: cation; hypercoordinated tin; pincer-type ligand.

The soft phosphane donor moiety has been used in organotin chemistry (Izod, 2012; Hupf et al., 2014). Yet, ionogenic compounds containing tin cations and phosphane Lewis bases are scarce (Barney et al., 1999; Objartel et al., 2008; MacDonald et al., 2011, 2012; Weicker et al., 2013; Burt et al., 2014). Recently, we reported the synthesis of and density functional theory (DFT) calculations on the heteroleptic organostannylene chromium pentacarbonyl complexes $[4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2(X)SnCr(CO)_5}]$ (X=ClO_4, OTf), and $[4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2(L)SnCr(CO)_5}][\mathrm{ClO_4}]$ (L=$p\mathrm{Me_2NC_5H_4N}$ (DMAP, 4-dimethylaminopyridine), Ph_3PO). Within the scope of these investigations, we also learned about the ability of the soft Lewis base triphenylphosphane, PPh_3 to stabilize such complexes but, at that time, failed isolating the corresponding representative (Wagner et al., 2013). Herein, we report the isolation and complete characterization of the triphenylphosphane-stabilized organostannylene chromium pentacarbonyl complex **2** (L=PPh_3, Scheme 1). Compound **2** might formally be rationalized as a push-pull complex (Thimer et al., 2009; Al-Rafia et al., 2011; Ghadwal et al., 2011; Swarnakar et al., 2014; El Ezzi et al., 2015). However, as it was demonstrated previously (Wagner et al., 2013), both the Sn-Cr and Sn-P bonds are highly covalent.

Compound **2** was obtained as a colorless crystalline material from a solution of the corresponding perchlorate salt **1** in acetonitrile to which an equimolar amount of PPh_3 had been added. Compound **2** shows good solubility in common polar organic solvents such as acetonitrile and dichloromethane.

The molecular structure of **2**, as well as selected interatomic distances and angles, is shown in Figure 1.

The Sn(1) atom is pentacoordinated and exhibits a trigonal-bipyramidal environment, where O(1) and O(2) occupy the axial and C(1), Cr(1), and P(3) the equatorial positions, respectively. The overall geometry is similar to that of the corresponding DMAP-stabilized derivative (Wagner et al., 2013). The Cr(1)-Sn(1)-C(1) angle of 138.00(7)° is smaller than in compound **1** (146.31(10)°) (Wagner et al., 2013). The Sn(1)-P(3) distance of 2.6665(7) Å in **2** is similar as the ones observed in $Sn(SCH_2CH_2)_2PPh$ [2.614(5) Å] (Baumeister et al., 1986), $[PhB(CH_2PPh_2)_3][SnCl]$ [2.6746(14) Å] (Barney et al., 1999) and $[(Ph_2Ppic)Sn(Cl)][SnCl_3]$ (pic=2-picolyl) [2.6962(5) Å] (Objartel et al., 2008). A shorter Sn-P distance was observed in $[SnCl_2(PMe_3)_2][AlCl_4]_2$ with 2.5390(6) Å (MacDonald et al., 2012). Similar and longer distances were also found for phosphane stannylene Lewis pairs [2.6362(6)–2.7489(4) Å] (Freitag et al., 2013a,b) and for $[PhP(CH_2CH_2S)_2Sn(C_5H_5N)Cr(CO)_5]$ [2.756(1) Å] (Jurkschat et al., 1988). For $[(o\mathrm{C_6H_4CH_2PPh_2})_2\mathrm{SnW(CO)_5}]$, the Sn-P distances of 2.831(2) and 3.012(2) Å are much longer, however (Abicht et al., 1987).

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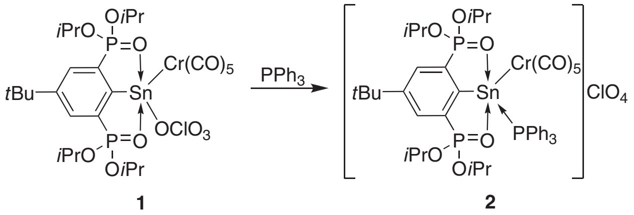


Scheme 1: Synthesis of the ionic compound **2** containing a triphenylphosphane-stabilized cationic organotin chromium pentacarbonyl complex.

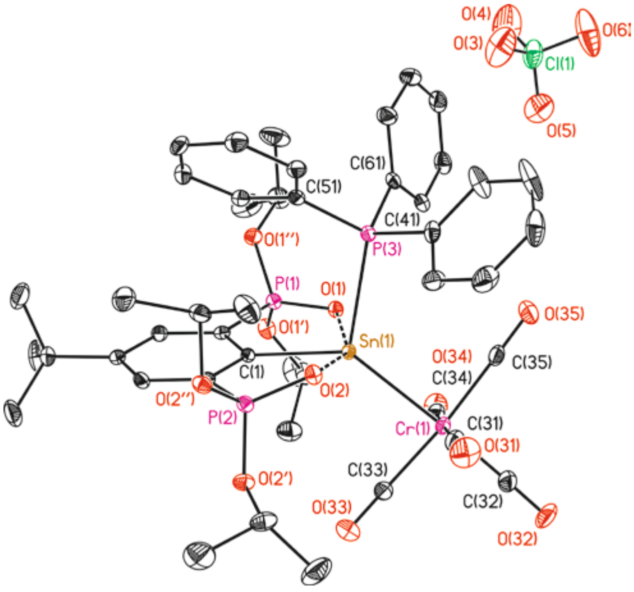


Figure 1: Molecular structure (SHELXTL) of **2** showing 30% probability displacement ellipsoids.
The hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn(1)-C(1) 2.176(3), Sn(1)-Cr(1) 2.5896(5), Sn(1)-P(3) 2.6665(7), Sn(1)-O(1) 2.3081(19), Sn(1)-O(2) 2.3471(19), Cr(1)-Sn(1)-C(1) 138.00(7), Cr(1)-Sn(1)-P(3) 119.30(2), C(1)-Sn(1)-P(3) 102.65(7), O(1)-Sn(1)-O(2) 152.18(7).

During storage of compound **2** in CD$_3$CN solution in a sealed NMR tube, yellow crystals separated. These were identified by single crystal X-ray diffraction as *trans*-[Cr(CO)$_4$(PPh$_3$)$_2$], **3**, which crystallized as a polymorph to known structures with similar interatomic distances and angles (Bao et al., 2001; Bennett et al., 2004). Compound **3** crystallized in the space group $P\bar{1}$ with two molecules in the unit cell. As for structures of *trans*-[Cr(CO)$_4$(PPh$_3$)$_2$] published before, a higher symmetry than $P\bar{1}$ is missing for all structures. The molecular structure of compound **3** is shown in Figure 2. Selected interatomic distances and angles are given in the figure caption.

A ^{31}P NMR spectrum of compound **3** in C$_6$D$_6$ showed a signal at δ 75.3 ppm being identical with that reported previously (Beck et al., 1994).

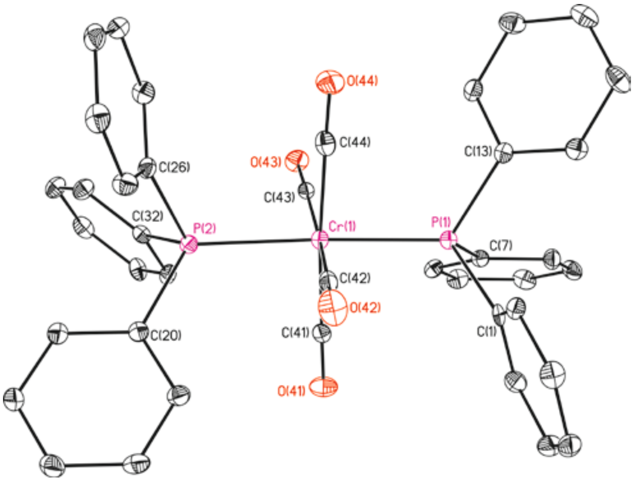
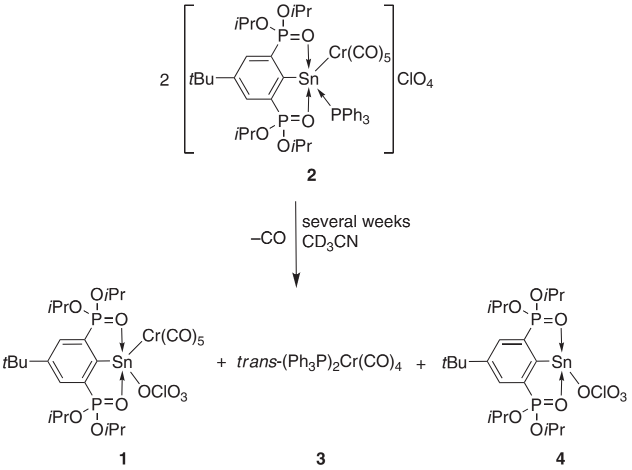


Figure 2: Molecular structure (SHELXTL) of *trans*-[Cr(CO)$_4$(PPh$_3$)$_2$], **3**, showing 30% probability displacement ellipsoids.
The hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): P(1)-Cr(1) 2.3298(10), P(2)-Cr(1) 2.3370(10), Cr(1)-C(41) 1.902(4), Cr(1)-C(44) 1.876(4), P(1)-Cr(1)-P(2) 177.65(4), C(42)-Cr(1)-C(43) 172.15(15).

A ^{31}P NMR spectrum of the CD$_3$CN solution from which the crystals of complex **3** had been separated showed two major resonances at δ 37.3 [$J(^{31}\text{P-}^{117/119}\text{Sn})=125/130$ Hz] and 30.3 ppm [$J(^{31}\text{P-}^{117/119}\text{Sn})=180$ Hz], respectively, in an almost 1:1 ratio. The first resonance is assigned to the organotin(II) perchlorate RSnOClO$_3$, **4** [R=4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$C$_6$H$_2$]. The chemical shift and magnitude of the coupling constant are close to the values reported for RSnCl [δ 37.8 ppm, $J(^{31}\text{P-}^{117/119}\text{Sn})=113/119$ Hz] (Henn et al., 2011). The second resonance is assigned to compound **1** (Wagner et al., 2013). A ^{1}H NMR spectrum showed two sets of signals for the aromatic protons of the ligand that are assigned to **1** and **4**, respectively. A ^{1}H ^{13}C HMBC spectrum showed cross peaks



Scheme 2: Reaction of compound **2** in the CD$_3$CN solution.

to the C(1) carbon atoms at δ 170.4, **1**, and δ 182.4 ppm, **4**. The low field shift of the C(1) signal, which is assigned to compound **4**, showed the absence of the transition metal fragment. A similar trend was observed for RSnCl [R=4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$C$_6$H$_2$] (δ 186.7 ppm) compared with RSn(Cl)Cr(CO)$_5$ (δ 171.7 ppm) (Henn et al., 2011).

The reaction according to Scheme 2 proceeds *via* nucleophilic attack of the kinetically labile triphenylphosphane at the chromium center (Scheme 2). The driving force for the formation of **3** is its low solubility in acetonitrile.

Experimental section

Crystallographic details

Intensity data for the crystals (**2**, **3**) were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 110 K (Table 1). The structures were solved with direct methods using SHELXS-97 (Sheldrick, 2008). Refinements were carried out against F^2 by using SHELXL-97 (Sheldrick, 2008). The C-H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. CCDC-1047815 (**2**) and -1047816 (**3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General

4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$C$_6$H$_2$Sn(ClO$_4$)Cr(CO)$_5$ (**1**) was prepared as described (Wagner et al., 2013). All reactions were performed under argon. The solvents including NMR solvents were destilled from the appropriate drying agent and stored over molecular sieve. The NMR tube was flame sealed. The NMR spectra were run on a Bruker DPX 300/DRX 500 or Varian Mercury spectrometer at room temperature. NMR chemical shifts are given in parts per million. The ^{1}H and ^{13}C NMR spectra were referenced to SiMe$_4$ using the solvent signal

Table 1: Crystallographic data.

	2	3
Empirical formula	$C_{45}H_{54}ClCrO_{15}P_3Sn$	$C_{40}H_{30}CrO_4P_2$
Formula weight (g/mol)	1133.93	688.58
T (K)	173(2)	173(2)
Crystal system	monoclinic	triclinic
Crystal size (mm)	0.30×0.14×0.06	0.50×0.15×0.08
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	18.2967(7)	10.2390(7)
b (Å)	13.3670(5)	12.2624(8)
c (Å)	21.9794(8)	14.7020(10)
α (°)	90	97.596(6)
β (°)	104.653(4)	106.237(6)
γ (°)	90	106.466(6)
V (Å^3)	5200.7(4)	1654.17(19)
Z	4	2
ρ_{calcd} (g/cm^3)	1.448	1.382
μ (mm^{-1})	0.895	0.485
F(000)	2320	712
θ range (°)	2.26–25.50	2.32–25.50
(hkl) ranges	$-22 \le h \le 22$	$-12 \le h \le 11$
	$-16 \le k \le 16$	$-14 \le k \le 13$
	$-26 \le l \le 26$	$-17 \le l \le 17$
Reflections collected	49117	13819
Completeness to θ_{max} (%)	99.9	99.9
Independent reflections/R_{int}	9672/0.0468	6167/0.0588
No. of reflections observed with [$I>2\sigma(I)$]	7781	3876
Absorption correction	Multi-scan	Multi-scan
T_{max}/T_{min}	1.0/0.95897	1.0/0.96412
Parameter	595	352
GoF(F^2)	1.134	0.984
R_1(F) [$I>2\sigma(I)$]	0.0342	0.0516
wR_2(F^2) (all data)	0.0926	0.1111
Largest difference peak and hole (e/Å^3)	1.160/-1.061	0.516/-0.441
CCDC number	1047815	1047816

(CD_3CN ^{1}H 1.94 ppm, ^{13}C 1.39 ppm). The NMR spectra were referenced to 85% $\mathrm{H_3PO_4}$ (^{31}P) and $\mathrm{SnMe_4}$ (^{119}Sn). The IR spectra (cm^{-1}) were measured as solids on an ATR Perkin Elmer Spectrum Two. The melting point was measured in an open capillary on a Büchi M-560. The electrospray mass spectra were run on a Thermoquest-Finnigan device using acetonitrile solutions with a concentration of 0.1 mg/mL and a flow rate of 10 µL/min. The experimental isotopic pattern matched the theoretical ones.

[2,6-Bis(di-*iso*-propoxyphosphonyl)-4-*tert*-butyl] phenyl}tin triphenylphosphane perchlorate chromium pentacarbonyl, $[\mathrm{4\text{-}}t\mathrm{Bu\text{-}2,6\text{-}\{P(O)(O}i\mathrm{Pr)_2\}_2C_6H_2Sn(PPh_3)Cr(CO)_5]ClO_4}$ (2)

Triphenylphosphane (51 mg, 0.19 mmol) was added to a solution of $[\mathrm{4\text{-}}t\mathrm{Bu\text{-}2,6\text{-}\{P(O)(O}i\mathrm{Pr)_2\}_2C_6H_2Sn(ClO_4)Cr(CO)_5]}$ (170 mg, 0.19 mmol) in $\mathrm{CH_3CN}$ (3 mL). After addition of toluene, colorless crystals were grown at 4°C, which were washed with toluene and dried *in vacuo*. Yield (86 mg, 39%); mp 138°C (decomp); ^{1}H NMR ($\mathrm{CD_3CN}$, 300.13 MHz): δ=1.11 [d, ${}^{3}J({}^{1}\mathrm{H}\text{-}{}^{1}\mathrm{H})$=6.2 Hz, 12H, $\mathrm{CH(C}H_3)_2$], 1.29 [d, ${}^{3}J({}^{1}\mathrm{H}\text{-}{}^{1}\mathrm{H})$=6.2 Hz, 12H, $\mathrm{CH(C}H_3)_2$], 1.41 [s, 9H, $\mathrm{C(C}H_3)_3$], 4.36–4.55 [not resolved, $\nu_{1/2}$=26 Hz, 4H, $\mathrm{C}H\mathrm{(CH_3)_2}$], 7.28 (br t, J=7.5 Hz, 6H, $\mathrm{Ph_3P}$), 7.42 (br t, J=7.6 Hz, 6H, $\mathrm{Ph_3P}$), 7.54 [br t, ${}^{3}J({}^{1}\mathrm{H}\text{-}{}^{1}\mathrm{H})$=7.6 Hz, 3H, *para*-$\mathrm{Ph_3P}$], 8.10 [pseudo-d, ${}^{3}J({}^{31}\mathrm{P}\text{-}{}^{1}\mathrm{H})$=14.6 Hz, 2H, $\mathrm{C}H_{\mathrm{aryl}}$]; ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$, 75.47 MHz): δ=23.8–23.9 [not resolved, $\mathrm{CH(}C\mathrm{H_3)_2}$], 23.9–24.1 [not resolved, $\mathrm{CH(}C\mathrm{H_3)_2}$], 31.2 [s, $\mathrm{C(}C\mathrm{H_3)_3}$], 36.1 [s, $C\mathrm{(CH_3)_3}$], 76.2 [complex pattern, $C\mathrm{H(CH_3)_2}$], 130.4 [d, $J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=9.4 Hz, $\mathrm{C_{PPh_3}}$], 132.4 [dd, ${}^{1}J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=188 Hz, ${}^{3}J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=18.9 Hz, $C_{\mathrm{2,6aryl}}$], 132.7 (br s, *para*-$\mathrm{C_{PPh_3}}$), 134.0 (dd, ${}^{2}J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=13.8 Hz, ${}^{4}J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=4.4 Hz, $C_{\mathrm{3,5aryl}}$], 134.8 [d, $J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=13.8 Hz, $\mathrm{C_{PPh_3}}$], 157.0 [t, ${}^{3}J({}^{13}\mathrm{C}\text{-}{}^{31}\mathrm{P})$=12.0 Hz, C_{4aryl}], 168.4 (complex pattern, C_{1aryl}), 219.0 [s, ${}^{2}J({}^{13}\mathrm{C}\text{-}{}^{117/119}\mathrm{Sn})$=116 Hz, CO_{cis}], 225.2 (s, CO_{trans}), *ipso*-$\mathrm{C_{PPh_3}}$ not found; ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$, 121.49 MHz): δ=28.5 [s, $J({}^{31}\mathrm{P}\text{-}{}^{117/119}\mathrm{Sn})$=168 Hz], 1.4 (s, $\nu_{1/2}$=95 Hz); IR (ATR): $\tilde{\nu}$ =2981 (CH), 2052 (CO), 1974 (CO), 1946 (CO), 1921 (CO), 1230, 1174, 1148, 1129, 1084, 983. Although single crystalline material was used for elemental analysis (under aerobic conditions), the values obtained differed by approximately 2%–6% from the calculated values.

Storage of $[\mathrm{4\text{-}}t\mathrm{Bu\text{-}2,6\text{-}\{P(O)(O}i\mathrm{Pr)_2\}_2C_6H_2Sn(PPh_3)Cr(CO)_5]ClO_4}$ (2)

A sample of $[\mathrm{4\text{-}}t\mathrm{Bu\text{-}2,6\text{-}\{P(O)(O}i\mathrm{Pr)_2\}_2C_6H_2Sn(PPh_3)Cr(CO)_5]ClO_4}$ in $\mathrm{CD_3CN}$ was stored in a sealed NMR tube for 10 weeks during which a few yellow crystals precipitated. The solution was checked NMR spectroscopically and the crystals were identified as *trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]$ *via* single crystal X-ray diffraction analysis.

${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$, 81.02 MHz): δ=55.7 (s, not assigned, integral 12), 37.3 [s, $J({}^{31}\mathrm{P}\text{-}{}^{117/119}\mathrm{Sn})$=125/130 Hz, **4**, integral 41], 30.3 [bs, $J({}^{31}\mathrm{P}\text{-}{}^{117/119}\mathrm{Sn})$=180 Hz, **1**, integral 38], 2.0 (bs, **$\mathrm{PPh_3}$**, integral 9); ^{13}C NMR ($\mathrm{CD_3CN}$, *g*HMBC 125.67/499.78 MHz): δ=182.4 (C_{1aryl}, **4**), 170.4 (C_{1aryl}, **1**), 134.3 ($C_{\mathrm{2,6aryl}}$, **4**), 133.5 ($C_{\mathrm{2,6aryl}}$, **4**); ^{1}H NMR ($\mathrm{CD_3CN}$, 499.79 MHz, signals that are not superimposed): δ=8.13 (br pseudo-*d*, $\mathrm{C}_{H\mathrm{aryl}}$, **1**, integral 0.92), 7.97 (pseudo-*d*, $\mathrm{C}_{H\mathrm{aryl}}$, **4**, integral 1.08); ${}^{119}\mathrm{Sn}\{{}^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$, 111.92 MHz): δ=-263 (bs, not assigned).

***trans*-$[\mathrm{Cr(CO)_4(PPh_3)_2}]$, 3:** ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 121.49 MHz): δ=75.3; IR (ATR): $\tilde{\nu}$ =1873 cm^{-1} (vs, CO), 1940 cm^{-1} (CO); ESI MS (+, $\mathrm{CH_3CN}$): *m/z*=631.1 $[\mathrm{M\text{-}Ph^{-}+H^{+}+H_3O^{+}}]^{+}$ (100%), 633.2 $[\mathrm{M\text{-}2CO+H^{+}}]^{+}$.

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