

Intramolecular Metalation of C–H Bonds with {*cis,cis*-1,3,5-Tris[(diphenylphosphino)methyl]cyclohexane}rhodium(I) Chloride

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The novel tridentate ligand *cis,cis*-1,3,5-tris[(diphenylphosphino)methyl]cyclohexane (**6**) has been synthesized and treated with [Rh(COD)Cl]₂. Intramolecular metalation of a C–H bond of the cyclohexane ring occurs (**7**). Studies with D₂ gas and **6**[D₆] prove that axial and equatorial C–H bonds are

metalated and that a mutual exchange occurs in this process. Replacement of the Cl[−] by the SbF₆[−] anion in **7** results in a reduced interaction between the metal and the C–H bond (**8**). **7** reacts with CO to form the carbonyl **9** where no such interaction is observed.

Ever since the inception of organometallic chemistry, the metalation of aliphatic and aromatic hydrocarbons (i. e. C–H is replaced by C–M) has been a goal generally sought after¹. One of the first examples of C–H metalation with non-transition metals was observed in 1962 when the cyclo-orthometalation of sp² C–H bonds during the heating of triphenylaluminum² and the metalation of azobenzene with nickelocene were realized³. In all of these cases the variable polarity of the C–M bonds offers many synthetic possibilities in heterogeneous catalysis, homogeneous catalysis and organic synthesis when selectivity and functionalization of the C–M bond can be achieved⁴.

The main features of the C–H metalation process with transition metals have been described in a number of theoretical^{5,6} and experimental papers^{7,8}. Specifically the process can be divided into the categories of intramolecular and intermolecular metalation. Normally, intramolecular metalation has a thermodynamic advantage over intermolecular C–H metalation⁹, which is probably the reason why so many instances of this type have been observed.

The specific details of C–H metalation are still quite controversial. Evidence has been presented for "agostic" interactions¹⁰, σ-complexation^{7b,11}, and η²-complexation^{7a}) all of which may play an important role in the metalation process. In our search for new materials which will metalate C–H bonds we have discovered a rhodium complex that illustrates some new aspects of the process. Thus, we have found that this intramolecular metalation process involves three steps each of these indicating that the rhodium-carbon bonding is extremely important in driving the metalation process to completion.

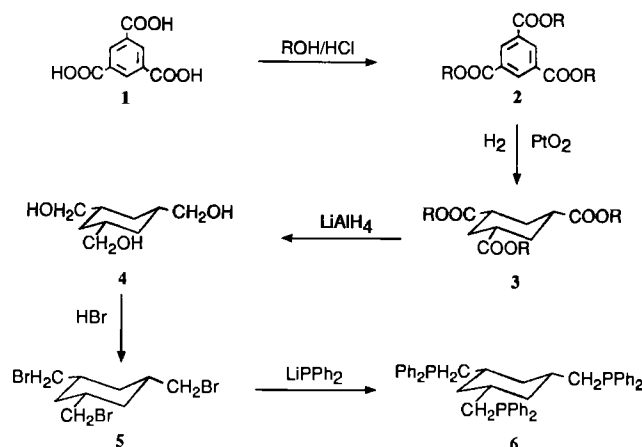
Results and Discussion

Ligand Synthesis

Hoffmann^{6a}) has suggested that ligands which force the coordination geometry of late transition metals to be py-

ramidal can control their d-orbitals for low-energy C–H metalation processes. To test this idea we have designed the new ligand *cis,cis*-1,3,5-tris[(diphenylphosphino)methyl]cyclohexane (**6**), which has been prepared by a five-step synthesis from trimesic acid (Scheme 1). The intermediates **1**–**5** have been described by others¹².

Scheme 1



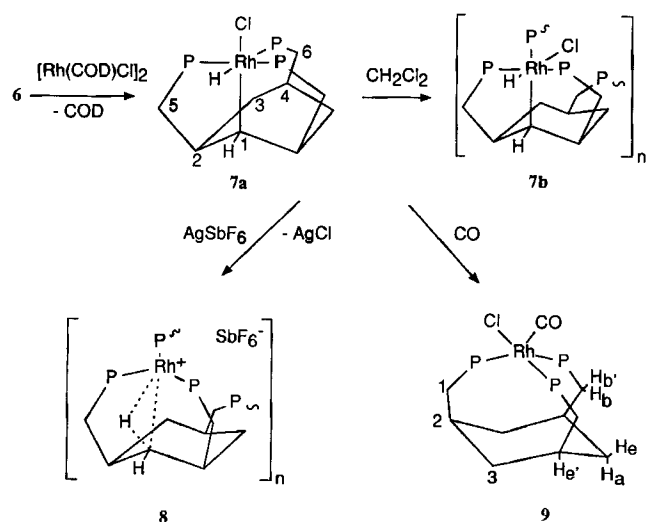
Treatment of *cis,cis*-1,3,5-tris(bromomethyl)cyclohexane (**5**) with an equimolar amount of LiPPh₂ in *n*-hexane results in **6** as a colorless solid, soluble in organic solvents. The ¹H-, ¹³C-, and ³¹P-NMR spectra of **6** confirm the *cis,cis*-configuration of the (diphenylphosphino)methyl groups in the 1,3,5-positions of the cyclohexane ring. Hence, **6** exhibits only one phosphane ³¹P{¹H}-NMR signal, three alkane ¹³C{¹H}-NMR signals each coupled to phosphorus, and four multiplet ¹H-NMR patterns consistent with the chair conformation of the cyclohexane ring¹². Deuteration of **2** with D₂ gas and PtO₂ as a catalyst quantitatively yields the triester **3**[D₆] with deuterium located stereospecifically on one

side of the ring. Thus, **6**[D₆] (Scheme 3) is obtained as the final phosphane, which has been characterized by ¹H-, ¹³C-, and ³¹P-NMR spectroscopy. Due to rotation of the (diphenylphosphino)methyl group around the C–C bond the three phosphorus atoms with their donating free electron pairs point towards the C₃ axis. Thus a metal atom can be located in a specific pyramidal arrangement above the cyclohexane ring.

Complexation

Treatment of **6** with [Rh(COD)Cl]₂ in hot toluene gives in almost quantitative yield a pale yellow solid **7** with complete displacement of cyclooctadiene (Scheme 2). Due to the lack of solubility all investigations have been carried out in dichloromethane. The ³¹P{¹H}-NMR spectrum displays the multiplet pattern of an A₂MX spin system, a doublet of doublets of intensity 2 at δ = 43.4 (*J*_{RhP} = 120.5, *J*_{PP} = 25.8 Hz) due to the *trans*-phosphorus nuclei and a doublet of triplets of intensity 1 at δ = 13.2 (*J*_{RhP} = 80.3, *J*_{PP} = 25.8 Hz) due to the phosphorus in the *cis*-position, which is consistent with a mirror-plane symmetry of **7**. This is also manifested in the ¹³C{¹H}-NMR spectrum which shows six distinct peaks in the alkane region at δ = 31.0 (C-6), 35.2 (C-4), 42.5 (C-5), 44.6 (C-3), 48.1 (C-2), 65.1 (C-1). The broad linewidth (30 Hz) prevents the observation of couplings to the phosphorus atoms in the case of C-2 to C-6. The signal of C-1 is split into a doublet of doublets (*J*_{RhC} = 17.1, *J*_{PC} = 85.5 Hz). Assignment of the resonances has been supported by distortionless enhancement polarization transfer NMR experiments (DEPT)¹³ and is consistent with the structure shown.

Scheme 2



Although **7** seems to be monomeric on the basis of mass spectrometrical data (fast atomic bombardment), molecular weight measurements in dichloromethane show an increase from monomer to oligomer over a period of minutes (**7b**). The strain in **7a** is released by opening one of the coordinated phosphane functions which, after rearrangement, is

again coordinated, but to another molecule *trans* to C-1. This is indicated by the large P–C interaction of C-1, which has been shown to be due to the phosphorus in the *cis*-position with respect to the pair of mutually *trans* phosphorus nuclei by selective ¹³C{¹H, ³¹P}-NMR experiments. Nevertheless, because the symmetry about C-1 is not changed, the same ¹H-, ¹³C-, and ³¹P-NMR spectra are obtained. This is supported by a CP/MAS ¹³C-NMR spectrum in the solid state. The tendency to form oligomers has frustrated attempts to grow crystals and causes the line shapes to become broadened. This effect also obscures the observation of fluxionality upon cooling of the complex.

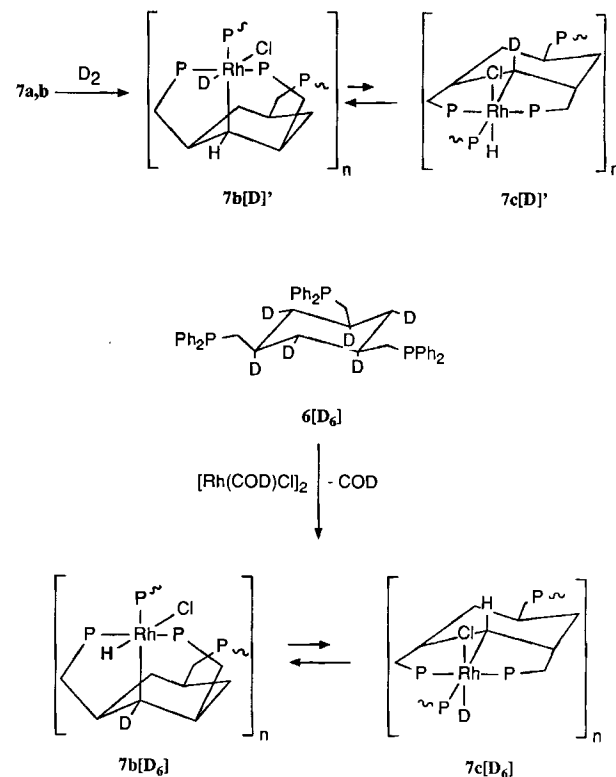
Evidence for the presence of a hydride is provided by the ¹H-NMR spectrum revealing a broad resonance (*v*_{1/2} > 50 Hz) at δ = –19.4, which is ascribed to a single proton by integration. There is no discernible coupling of the hydrogen atom to the rhodium or the phosphorus nuclei. The formation of the hydride is an intramolecular process, as the reaction in [D₈]toluene leads to the same ¹H-NMR spectrum.

Rhodium-hydrogen interaction is also revealed by a broad band at 2085 cm^{–1} in the IR spectrum. We have not been able to observe the *v*(Rh–Cl) stretching frequency.

Exchange Experiments

Treatment of **7** in CD₂Cl₂ with an excess of D₂ gas at 2 atm causes the *v*(Rh–H) stretching vibrations as well as the hydride resonance in the ¹H-NMR spectrum to disappear proving intermolecular exchange of Rh–H for Rh–D. However, besides the expected resonance at high field an

Scheme 3



additional broad peak at $\delta = 1.9$ in the ^2H -NMR spectrum indicates the incorporation of deuterium into the cyclohexane skeleton (Scheme 3). The reverse case, namely the transfer of a deuterium atom from the cyclohexane ring to the metal, is observed when **6**[D_6] is treated with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (Scheme 3). This is demonstrated by the characteristic hydride peak in the ^2H -NMR spectrum which leads to a diminished hydride resonance in the ^1H -NMR spectrum. These data suggest that both the axial and the equatorial C–H bond can be oxidatively added to the P–Rh–P moiety. The exchange on both sides of the ring (Scheme 3) is too slow to be studied by NMR techniques.

Cationic Rhodium Complex

Replacement of chlorine by the non-coordinating ligand SbF_6^- leaves the metal with a positive charge (Scheme 2). Therefore, we observe a reduced interaction of the metal with the C–H bonds, which is indicated by the hydride resonance at $\delta = -2.6$ and thus shifted to lower field compared to **7**. This is in agreement with the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum, which displays six resonances in the alkane region. The α -methylene carbon atoms (C-5, C-6) are not distinguishable and resonate at $\delta = 46.0$, whereas the signal of the methine group (C-2) is shifted to higher field ($\delta = 34.5$), close to the methine carbon (C-4) resonance at $\delta = 33.1$. The most dramatic shift is observed for C-1, which in the case of **8** gives rise to a doublet at $\delta = 36.6$ ($J = 23.8$ Hz). This splitting is most likely due to a *trans*-C–Rh–P interaction similar to **7** but greatly reduced. Consequently the Rh–C coupling is too small to be observed with the line broadening present. In contrast to **7** this carbon atom behaves as a methylene group in a DEPT¹³ experiment. The tendency of smaller shift separation between the carbon atoms is also observed in the ^{31}P -NMR spectrum which consists of a broad doublet of doubles at $\delta = 35.4$ ($J_{\text{RhP}} = 135.7$, $J_{\text{PP}} = 29.9$ Hz) and a broad doublet of triplets at $\delta = 27.1$ ($J_{\text{RhP}} = 205.6$, $J_{\text{PP}} = 29.9$ Hz). This implies that the rhodium atom is arranged more symmetrically with respect to the cyclohexane ring.

The infrared spectrum shows no rhodium hydride peak and establishes the non-coordinative character of the SbF_6^- anion, since there is only one characteristic intensive absorption at 658 cm^{-1} .

Interaction of the Rhodium Chloride **7** with CO

Treatment of **7** with carbon monoxide at 1 atm in dichloromethane leads to a bright yellow solution containing, according to variable temperature ^{31}P -NMR spectroscopy, a complex-exchanging system. Removal of the carbon monoxide atmosphere and addition of *n*-hexane gives a bright yellow precipitate at low temperature identified as **9** (Scheme 2). The doublet in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum at $\delta = 28.9$ ($J_{\text{RhP}} = 126.5$ Hz) is invariable to changes of temperature in the range of 25 to -95°C which suggests a rapid fluxional process. Broad singlets at $\delta = 34.5$ (C-1), 36.8 (C-2), 43.4 (C-3) in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum are consistent with an exchanging system generating pseudo C_{3v} symmetry¹⁴. As the temperature is lowered the peaks become sharper dis-

playing multiplet patterns for C-1 and C-3 while C-2 remains a singlet.

The room-temperature ^1H -NMR spectrum shows no resonance due to interaction with the metal while the alkane region displays a doublet of triplets at $\delta = 0.55$ (H_a) and broad peaks at $\delta = 2.04$ (H_c , H_b), 2.62 (H_e), and 2.80 (H_b), respectively. This assignment has been confirmed by a 2D-COSY- ^1H -NMR experiment¹³. The chemical shift difference between the hydrogens H_b and H_c is attributed to a twist of the methylene bridges which generates different environments for the geminal protons.

The IR spectrum exhibits $\nu(\text{CO})$ at 1966 cm^{-1} and the far infrared $\nu(\text{RhCl})$ at 306 cm^{-1} . This is in agreement with a five-coordinate complex of this type¹⁵.

The chemistry and reactivity of the carbonyl complex are currently under investigation.

Conclusion

The synthesis of **6** and its complexation to a Rh–Cl fragment have produced a complex which depicts the metalation (intramolecular) of a saturated C–H bond. We characterize three stages of C–H metalation by the structures **7**, **8**, and **9**. In each case the C–H bond seems to move as the rhodium-carbon interaction changes which is evident by the way the three phosphorus atoms appear with respect to the rhodium nucleus. The presence of a rhodium-carbon interaction and a rhodium-hydrogen bond in two major modifications of the molecule as well as the subsequent loss of these interactions in the rhodium carbonyl complex indicate that metal-carbon bonding is extremely important in driving metalation reactions to completion.

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Experimental

All manipulations were performed under pure argon by using standard Schlenk methods. All deuterated solvents were distilled in vacuo from LiAlD_4 and stored in a vacuum atmosphere glove box under argon. Dichloromethane (Aldrich chromatography quality) was distilled from a small amount of LiAlH_4 . All other solvents were distilled from benzophenone ketyl which was generated by using a small amount of triglyme. Silver hexafluoroantimonate (Strem) was used as received. — IR: nujol mulls or KBr disks, Bio-Rad FTS-60 spectrometer. — MS: BG 70-250HF double focusing mass spectrometer. — Elemental analyses: Analytische Laboratorien, D-5250 Engelskirchen, and Institut für Anorganische Chemie, Tübingen. — NMR: GE 500 for ^1H (500.12 MHz), ^{31}P (202.47), and ^{13}C (125.7 MHz); a NT-300 spectrometer for ^1H (300 MHz), ^{31}P (121.4 MHz), and ^{13}C (75.4 MHz), and a Bruker AC 300 for ^{13}C (75.4 MHz).

cis,cis-1,3,5-Tris[(diphenylphosphino)methyl]cyclohexane (6): An ice-cooled solution of 5.57 g (30 mmol) of diphenylphosphane in 100 ml of *n*-hexane was treated with 17.6 ml of a 1.68 M solution

of *n*-BuLi/*n*-hexane. The yellow suspension was allowed to warm to room temp. After stirring for 3 h 3.6 g (10 mmol) of **5** dissolved in toluene was added dropwise. After stirring for 5 h the solution was hydrolyzed, the organic layer separated and dried with silica gel. Removal of the solvent and recrystallization of the residue from ether gave colorless crystals. Yield 4.5 g (66%), m.p. 106 °C (ether). — ¹H NMR (C₆D₆): δ = 0.75 (dt, ²J_{HH} = 12.0, ³J_{HH} = 12.0 Hz, 3H, CH_aH_b), 1.24–1.35 (m, 3H, CH_aCH₂P), 1.93 (d, ³J_{HH} = 7.0 Hz, 6H, CH₂P), 2.26 (br. d, ³J_{HH} = 12.0 Hz, 3H, CH_aH_b), 7.0–7.11 (m, 18H, *m,p*-H C₆H₅), 7.39–7.5 (m, 12H, *o*-H C₆H₅). — ¹³C{¹H} NMR (CDCl₃): δ = 34.9 (d, ²J_{PC} = 13.6 Hz, CHCH₂P), 36.4 (d, ¹J_{PC} = 12.7 Hz, CH₂P), 42.8 (t, ³J_{PC} = 9.7 Hz, CHCH₂CH), 128.3 (s, C-4 C₆H₅), 128.4 (s C-3,5 C₆H₅), 132.7 (d, ²J_{PC} = 18.6 Hz, C-2,3 C₆H₅), 139.0 (d, ¹J_{PC} = 12.1 Hz, C-1 C₆H₅). — ³¹P{¹H} NMR (CDCl₃): δ = –21.3 (s). — MS (70 eV): *m/z* (%) = 678 (13) [M⁺], 601 (12) [M⁺ – C₆H₅], 493 (10) [M⁺ – (C₆H₅)₂P], 183 (63) [M⁺ – CH₂C₆H₉[CH₂P(C₆H₅)₂]].

C₄₅H₄₅P₃ (678.8) Calcd. C 79.63 H 6.68
Found C 79.37 H 6.85

*cis,cis-1,3,5-Tris[(diphenylphosphino)methyl]cyclohexane*rhodium(III) Chloride (**7**): In a typical run 350 mg (0.52 mmol) of **6** and 121 mg (0.26 mmol) of [Rh(COD)Cl]₂ were heated in 50 ml of toluene to 90 °C with stirring for 3 h. After stirring at room temp. for 1 h the formed precipitate was filtered and washed with toluene and pentane. Yield 354 mg (83%), m.p. > 190 °C (dec.). — IR (KBr): $\tilde{\nu}$ = 2085 cm⁻¹ (Rh–H). — ¹H NMR (CD₂Cl₂): δ = –19.4 (br. s, 1H, RhH), –0.8–3.2 (br. m, 14H, aliphatic H), 6.4–7.8 (m, 30H, aromatic H). — ¹³C{¹H} NMR (CD₂Cl₂): δ = 31.0 (s, C-6), 35.2 (s, C-4), 42.5 (s, C-5), 44.6 (s, C-3), 48.1 (s, C-2), 65.1 (dd, ¹J_{RhC} = 17.1, ²J_{PC} = 85.5 Hz, C-1), 127.2–140.6 (br. m, C₆H₅). — ³¹P{¹H} NMR (CD₂Cl₂): δ = 13.2 (dt, ¹J_{RhP} = 80.3, ²J_{PP} = 25.8 Hz, 1 P, *cis*-P), 43.4 (dd, ¹J_{RhP} = 120.5, ²J_{PP} = 25.8 Hz, *trans*-P). — MS (FAB): *m/z* = 780 [Rh(PPh₂CH₂)₃C₆H₅]⁺.

C₄₅H₄₅ClP₃Rh (817.1) Calcd. C 66.15 H 5.55 Cl 4.34
Found¹⁶⁾ C 65.02 H 5.98 Cl 4.59

*cis,cis-1,3,5-Tris[(diphenylphosphino)methyl]cyclohexane*rhodium(III) Hexafluoroantimonate (**8**): To 85.9 mg (105 mmol) of **7** in 20 ml of dichloromethane 36.1 mg (105 mmol) of AgSbF₆ dissolved in 20 ml of dichloromethane was added dropwise at 0 °C. After the mixture was allowed to warm to room temp. over a 45-min period, the precipitate was filtered and the solvent evaporated. Yield quantitative, m.p. > 202 °C (dec.). — IR (KBr): $\tilde{\nu}$ = 658 cm⁻¹ (SbF₆⁻). — ¹H NMR (CD₂Cl₂): δ = –2.6 (br. s, RhH), –0.8–3.1 (br. m, 14H, aliphatic H), 6.8–8.0 (br. m, 30H, Ph). — ¹³C{¹H} NMR (CD₂Cl₂): δ = 33.1 (s, C-4), 34.5 (s, C-2), 36.6 (d, *J* = 23.8 Hz, C-1), 39.6 (s, C-3), 46.0 (s, C-5, C-6). — ³¹P{¹H} NMR (CD₂Cl₂): δ = 27.1 (dt, 1 P, ¹J_{RhP} = 205.6, ²J_{PP} = 29.9 Hz, *cis*-P), 35.4 (dd, 2 P, ¹J_{RhP} = 135.7, ²J_{PP} = 29.9 Hz, *trans*-P). — MS (FAB): *m/z* = 780 [Rh(PPh₂CH₂)₃C₆H₅]⁺.

C₄₅H₄₅F₆P₃RhSb (1017.4) Calcd. C 53.12 H 4.46 F 11.20
Found¹⁶⁾ C 52.49 H 4.67 F 10.39

Carbonyl{*cis,cis-1,3,5-tris[(diphenylphosphino)methyl]cyclohexane*rhodium(I) Chloride (**9**): The argon gas over the solution of 150 mg (0.184 mmol) of **7** in dichloromethane was replaced by carbon monoxide according to the freeze-thaw-pump method, and the solution was stirred for 16 h. Treatment with *n*-hexane afforded a precipitate which was filtered and washed with pentane and recrystallized from dichloromethane/*n*-hexane. Yield 112 mg (71%), m.p. > 225 °C (dec.). — IR (KBr): $\tilde{\nu}$ = 1966 cm⁻¹ (CO), 306 (RhCl). — ¹H NMR (CD₂Cl₂): δ = 0.55 (dt, ²J_{HH} = 12.0, ³J_{HH} = 11.5 Hz, 1H, CH_aH_b), 2.04 (br. s, 1H, CHCH₂P), 2.04 (br. s, 1H, CH₂P), 2.62 (br. s, 1H, CH_aH_b), 2.80 (br. s, 1H, CH₂P). — ¹³C{¹H}

NMR (CD₂Cl₂, –35 °C): δ = 34.5 (dd, ²J_{RhC} = 13.5, ¹J_{PC} = 13.5 Hz, C-1), 36.8 (s, C-2), 43.4 (t, ³J_{PC} = 8.7 Hz, C-3). — ³¹P{¹H} NMR (CD₂Cl₂) = 28.9 (d, ¹J_{RhP} = 126.5 Hz).

C₄₆H₄₅ClOP₃Rh (845.2) Calcd. C 65.37 H 5.37 Cl 4.19
Found¹⁶⁾ C 64.13 H 5.39 Cl 4.17

CAS Registry Numbers

2 (R = Me): 2672-58-4 / **3**[D₆]: 127761-91-5 / **5**: 65672-58-4 / **6**: 127761-93-7 / **6**[D₆]: 127761-92-6 / **7a**: 127761-94-8 / **7b**: 127762-00-9 / **7b**[D₆]: 127761-98-2 / **7c**[D₆]: 127761-99-3 / **8**: 127761-96-0 / **9**: 127761-97-1 / HPPH₂: 829-85-6 / [Rh(COD)Cl]₂: 12092-47-6 / AgSbF₆: 26042-64-8

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[94/90]