Organometallic Group-13 Metal Complexes of d-Block Elements, XIV[◇]

Intramolecularly Base-Adduct-Stabilized Transition-Metal-Substituted Indanes: Synthesis and Spectroscopic Characterization, Structure of $(\eta^5\text{-}C_5H_5)(CO)Ni{-}InBr_2(NC_7H_{13})$

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The reaction of $InBr/InBr_3$ or $InBr/BrIn[(CH_2)_3NMe_2]_2$ with the transition metal dimers $[L(CO)_nM]_2$ {L = CO, Cp, $C_5H_4[(CH_2)_2NMe_2]$; M = Fe, Co, Ni; $n = 1-3$} in THF or dioxane gives in almost quantitative yield the transition metal indium complexes $L(CO)_nM{-}InBr_2(Do)$ (Do = THF, NC_7H_{13}) and $L(CO)_nM{-}In[(CH_2)_3NMe_2](Br)$ respectively. The new compounds were characterized by elemental analysis, infrared ν(CO) spectroscopy, NMR, and mass spectrometry. An X-ray single crystal structure determination of $(\eta^5\text{-}C_5H_5)(CO)Ni{-}InBr_2(NC_7H_{13})$ (**1a**) revealed a short Ni–In bond of 246.3(1) pm.

The chemistry of transition metal indium compounds has a long tradition and dates back to the early work of W. Hieber and U. Teller on $In[Co(CO)_4]_3$[1] in 1942. Other more recent work deals with compounds of groups 6–8, e.g. $[L(CO)_nM]_mInX_{3-m}(Do)$ (M = d-block element; L = CO, Cp, PPh_3; $n = 1-4$; $m = 1-3$; X = Cl, Br, I; L = THF, py or other Lewis donors)[2,3]. The majority of those complexes can be viewed as derivatives of indium trihalides, $(L_nM)_mInX_{3-m}$. In contrast to this, very few compounds exist with an indium center bearing alkyl groups such as $[Cp(CO)_3M]_2In[(CH_2)_3NMe_2]$ (M = Mo, W) and $L(CO)_nM{-}In[(CH_2)_3NMe_2]_2$ (M = Mn, Re, Co, L = CO; n = 4, 3; M = Fe, Ni; L = Cp; n = 2–1)[4], *mer*-$\{[(CH_3)_3P]_3(H)(C_2H_5)Ir{-}In(C_2H_5)_2\}$[5] and *cis*-$[(Cy_2PCH_2CH_2PCy_2)\{(CH_3)_3SiCH_2\}Pt{-}In\{CH_2Si(CH_3)_3\}_2]$ (Cy = *cyclo*-C_6H_{11})[6]. However, some of those alkylindium transition metal complexes are sufficiently volatile and have been shown to serve as single-molecule precursors for the growth of the respective phase-pure thin alloy films by organometallic chemical vapor deposition (OMCVD), for example ε-NiIn from $Cp(CO)Ni{-}In[(CH_2)_3NMe_2]_2$[7]. In this paper we report on the synthesis and the characterization of some new (intramolecularly adduct-stabilized) transition metal-substituted indanes.

Results and Discussion

Treatment of a deep red-brown solution of $[Cp(CO)Ni]_2$ in THF with an equimolar amount (based on indium) of an 1:1 mixture of InBr and $InBr_3$ at reflux for 4 h gave a dark brown solution over traces of a non-identified precipitate. Addition of one equivalent of quinuclidine and recrystallization from THF/*n*-pentane afforded well-shaped *orthorhombic* crystals of **1a** (62% yield). The Lewis donor-functionalized nickel dimer $[Cp^N(CO)Ni]_2$ {$Cp^N = C_5H_4[(CH_2)_2NMe_2]$}[8] reacts similarly to give **1b**, the intramolecularly base adduct-stabilized congener of **1a**. Compounds **2**, **3** of Scheme 1, Table 1 were synthesized by analogous procedures.

A number of related compounds of the general type $L(CO)_nM{-}InX_2(Do)$ had been reported previously[2–3]. These compounds were synthesized by salt elimination from $[L(CO)_nM](Na/K)$, insertion of In^IX into M–X bonds of $L(CO)_nM{-}X$ or by reaction of the dimer with an *excess* of In^IX. However, those common methods suffer from several disadvantages which may lower the yield with respect to both metals substantially, down to 30–40% in certain cases[2–3]. The insertion reactions are sometimes accompanied by unwanted redox side reactions. Also, the success of the synthesis depends on the reaction conditions, in particular on the choice of the solvent[9a]. Moreover, the transition metal starting complexes $[L(CO)_nM](Na/K)$ or $L(CO)_nM{-}X$ are usually derived from the *dimers* $[L(CO)_nM]_2$, adding one synthetic step, which is especially detrimental, if a somewhat more precious ligand L is involved (e.g. Cp^N). Also, salt elimination reactions are often complicated by "ate-complex" formation. This is indicated, for example, by the reaction of **1a** with Z^+Br^- to give $[Cp(CO)Ni{-}InBr_3][Z]$ (**1c**: Z = $[HNC_7H_{13}]^+$ **1d**: Z = Ph_4P^+). **1c** was formed as a minor byproduct (*monoclinic* crystals) in the synthesis of **1a** and its structure was verified by X-ray single-crystal structure determination (see Experimental).

[◇] Part XIII: See ref.[10].

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All the above-mentioned problems can be avoided by using a simplified *one-step* method. A 1:1 mixture of InBr/InBr$_3$ is used as a synthetic equivalent of In$_2$X$_4$. Attempts to use isolated [In$_2$X$_4$ · Me$_2$N(CH$_2$)$_2$NMe$_2$][9b] in order to transfer an InBr$_2$ unit failed. We suppose that in the first step of the reaction InBr inserts into the metal-metal bond of the dimers [L(CO)$_n$M]$_2$. In the second step InBr$_3$ synproportionates with the resulting trinuclear complexes [L$_n$M]$_2$InBr via (solvent-dependent) dissociation/association equilibria to form the binuclear complexes **1b**, **2**–**3**. As expected, the Ni complex **4** is formed by using In^{I}Br alone. A quantitative Br/I exchange is achieved by treatment of the bromide compounds with an excess of sodium iodide in THF, e.g. the synthesis of **3a** (see Experimental). This is important if the starting compounds L(CO)$_n$M–I are used, which are often more easily derived than the Cl or Br derivatives. Thus, formation of a statistic mixture of halide substituents at the moiety InX$_a$I$_b$ (X ≠ I: $a + b = 2$) of the compounds **1**–**3** can be avoided.

Scheme 1

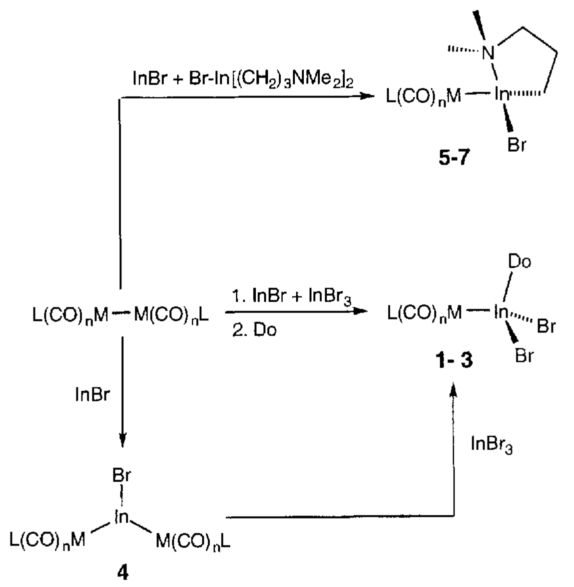


Table 1. Numbering scheme of the complexes **1**–**7** (Scheme 1)[a]

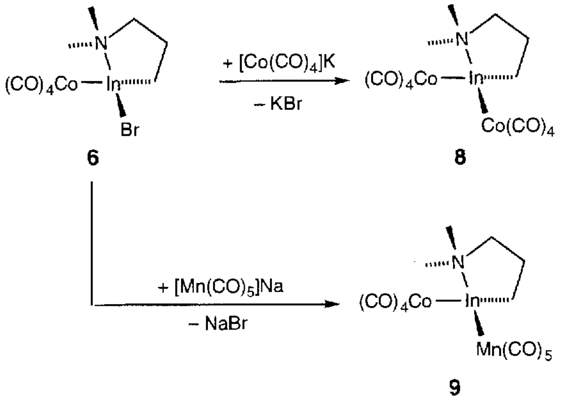
Compound	1a	1b	2	3	4	5	6	7
L	Cp	Cp^N	CO	Cp	Cp	Cp	CO	Cp
n	1	1	3	2	1	2	3	1
M	Ni	Ni	Co	Fe	Ni	Fe	Co	Ni
Do	Q	[b]	Q	Q	–	–	–	–

[a] Cp = η^5-C$_5$H$_5$; Cp^N = η^5:μ^1-{(C$_5$H$_4$)[(CH$_2$)$_2$NMe$_2$]}; Q = quinuclidine, NC$_7$H$_{13}$. – [b] See Figure 2.

An alkylation of the transition metal-substituted indium halides [L(CO)$_n$M]$_m$InX$_{3-m}$(Do) with conventional methods (alkyllithium reagents or alkyl Grignard reagents) is possible (as indicated by the expected shifts of the ν(CO) bands to lower wave numbers). But those reactions to obtain **5**–**7** are not very clean and selective, the yields are poor, and the products are difficult to purify. Instead, the smooth, redox-neutral and solvent-independent alkyl exchange between indium centers proved to be a very efficient strategy to introduce the desired dimethylaminopropyl substituent as exemplified by the synthesis of **6** (Scheme 1). Again, a 1:1 mixture of InBr/BrIn[(CH$_2$)$_3$NMe$_2$]$_2$ was used, which behaves as a synthetic equivalent of [BrIn{(CH$_2$)$_3$NMe$_2$}]$_2$. However, we could not isolate this proposed In^{II} intermediate. A 1:1 mixture of InBr and BrIn[(CH$_2$)$_3$NMe$_2$]$_2$ was heated at reflux for 12 h in toluene. Besides much elemental indium deposited in the reaction flask only the dialkyl fragment {In[(CH$_2$)$_3$NMe$_2$]$_2^+$, *m/z*: 287} could be detected by mass spectrometry. The selective alkylation of L(CO)$_n$M–InBr$_2$(Do) or [L(CO)$_n$M]$_2$InBr with BrIn[(CH$_2$)$_3$NMe$_2$]$_2$ or In[(CH$_2$)$_3$NMe$_2$]$_3$ to yield **5** and **7** is possible as judged by spectroscopic means (e.g. NMR, IR), but we did not attempt to obtain analytically pure samples from these reactions. Interestingly, the sequence of addition of the reactants is crucial to obtain a high yield of the desired mixed substituted alkyl complexes (see Experimental).

The residual bromide functionality of **6** can be exchanged by treatment with transition metal nucleophiles, yielding the trinuclear compounds **8**–**9**, for example (Scheme 2). Complex **9** constitutes the first mixed metalated alkylindium compound. The attempt to selectively alkylate **6** with alkyllithium reagents, e.g. methyllithium in THF solution, resulted in cleavage of the Co–In bond, which was indicated by the characteristic ν(CO) IR absorption at 1880 cm^{-1} (THF) of the anion [Co(CO)$_4^-$]. The corresponding alkylindium species could not be isolated. However, by extraction of this crude product mixture with toluene a yellow solution was obtained, which showed the expected ν(CO) IR absorptions of the desired intramolecularly adduct-stabilized *dialkylated* Co–In complex, (CO)$_4$Co–In[(CH$_2$)$_3$NMe$_2$](Me) (the indium analog of the related gallium complex[10]), but an analytically pure complex could not be isolated so far.

Scheme 2

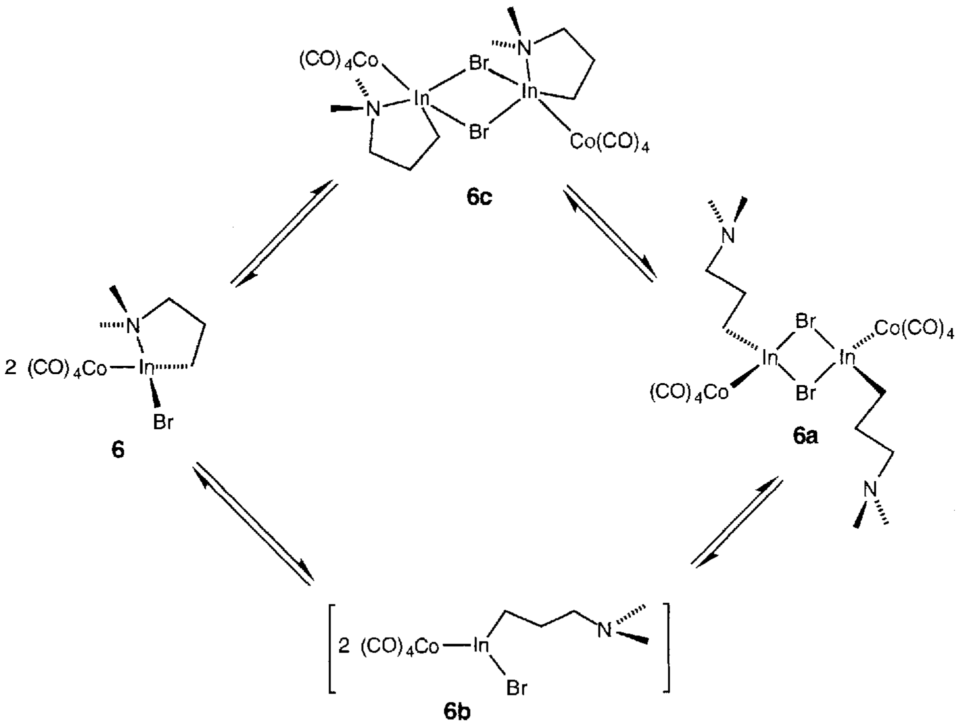


Spectroscopic Characterization

Dynamic NMR Studies

The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of compounds **1a**–**d**, **2**–**4**, and **8**–**9** are simple and without any unusual features. In the case of the Co–In compound **6** the ^{1}H-

Scheme 3



NMR spectra are comparatively complex and show interesting temperature-dependent dynamic effects of the dimethylaminopropyl ligand (Figure 1). The N-CH_3 groups of **6** are diastereotopic if the adduct ring is closed and the indium center is chiral. Higher temperatures favor the opening of the ring and thus the exchange of both N-CH_3 positions. This effect leads to the coalescence of the signals of the N-CH_3 groups in the NMR spectra and therefore allows the study of the Lewis base adduct dynamics in these complexes. By means of ^1H steady-state spin saturation of the diastereotopic N-methyl groups of **6** an exchange was found with a N-methyl group-containing species resonating at $\delta = 1.88$ present in low concentration. Since a singlet arising from the N-methyl groups appears even at very low temperatures (ca. −90 °C) it can be ruled out that this species forms an In−N heterocycle. We suspected that the dimer **6a** is responsible for the singlet at $\delta = 1.88$. Both configurational forms (*E*, *Z*) are expected to show singlets for the N-methyl groups and the chemical shift difference is probably too small to be resolved. Solvent-free L_nM-InX_2 complexes exhibit related dimeric structures in the solid state[2,3]. In non-coordinating solvents (toluene) those dimeric structures may be preserved, while they are broken up by donor solvents (THF).

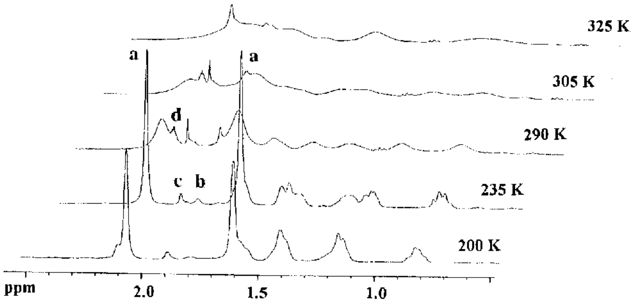
Complex **6** offers the opportunity to study this process by NMR spectroscopy. To test these assumptions, solutions with different concentrations of **6** were prepared and ^1H- and $^{13}C\{^1H\}$-NMR spectra were measured at various temperatures. The ratio of **6**/**6a** is lowered when the concentration of **6** is enlarged (Table 2). This result is derived from the integration ratio of the characteristic N-methyl groups of **6** and **6a**. This constitutes rather strong evidence for the monomer (**6**)/dimer (**6a**) equilibrium via **6c** of Scheme 3. Interestingly, the coalescence temperature of the N-methyl groups (^{13}C-NMR) depends inversely on the concentration (Table 2). This effect can be explained in the following way. The dimer formation (**6a**) and the subsequent dissociation of the In−N donor-acceptor bond [presumably via a short-lived five-coordinate indium species **6c** with a $NIn(\mu\text{-}Br)_2In'N'$ unit], resulting in the statistic exchange of the diastereotopic N-CH_3 groups, is much faster than the alternative N-CH_3 exchange involving the hypothetical low-coordinate monomeric form **6b**. In summary, these findings show, that the observed magnetic equivalence of the N-CH_3 groups at ambient temperature is best explained by a rather rapid *bimolecular* mechanism, leading to an equilibrium mixture of **6**/**6a**, **6** being the major species in solution.

The dimethylaminoethyl substituent of the cyclopentadienyl ligand of compound **1b** (Figure 2) is also coordinated to the indium center, again forming a Lewis base adduct. This is indicated by the ^1H-NMR spectrum which shows an AA'BB' spin system for each methylene group of the alkylamino substituent. The magnetic equivalence for the N-CH_3 groups observed at ambient temperatures may be explained by similar arguments as discussed above for **6**.

ν(CO) IR Studies

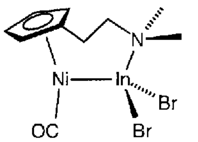
A comparison of the ν(CO) IR absorptions between the dihalo transition metal indidum complexes and the related dialkylated species L_nM-InR_2 ($R = (CH_2)_3NMe_2$)[4] shows clearly the stronger electron-withdrawing effect of the two bromine substituents at the indium center as compared to the two alkyl groups. The ν(CO) bands are shifted by nearly

Figure 1. ^{1}H-NMR spectra of **6** at various temperatures (in [D$_8$]-toluene, c = 0.44 mol/l)



[a] Signals of the diastereotopic *N*-methyl groups of **6**. – [b] Signals of the *N*-methyl groups of **6a**. – [c] Unknown impurity. – [d] Methyl group of [D$_8$]toluene.

Figure 2. Schematic representation of the structure of **1b**



1b

Table 2. ^{1}H- and ^{13}C-NMR data of **6** (in [D$_8$]toluene) at various temperatures and concentrations

c_{tot} [mol · l^{-1}]	**[6]/[6a]**	T_c[b] [K]	$\Delta G^{\neq}$[c] [kJ · mol^{-1}]
0.05	1.00/0.00 (274 K)[a]		
0.44	1.00/0.04 (274 K)	366	66.4 ± 0.2
1.10	1.00/0.15 (225 K)	303	59.6 ± 0.2
2.15	1.00/0.25 (210 K)	282	55.3 ± 0.2

[a] The temperatures in brackets refer to the spectra with the best resolution of the characteristic signals of the N-methyl groups. – [b] ^{13}C NMR. – [c] $\Delta\nu$ (Hz) = 330 Hz (^{13}C-NMR).

40–50 cm^{-1} to *higher* wave numbers in the case of **1a–d** and **2–4** as compared with **5–7**. The type of the donor ligand Do is less important. The exchange of quinuclidine for the weaker donor THF does not change the spectrum.

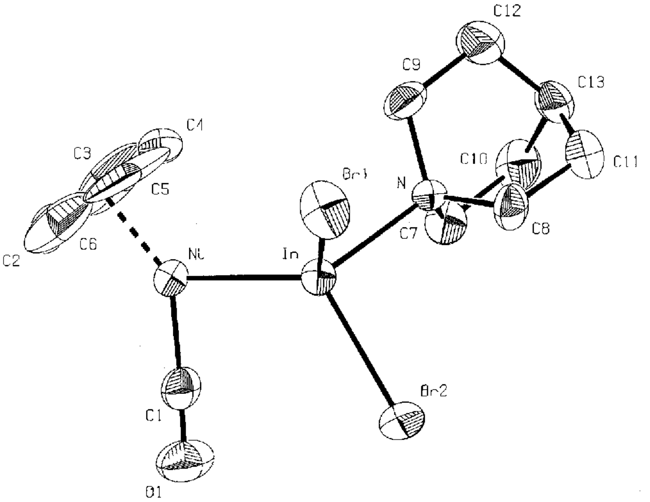
Mass Spectrometry

The mass spectra (EI, CI, FI) of dialkylindium transition metal carbonyl complexes usually show the fragment [InR_2^+] as the base peak. Fragments with higher masses and intact M–In (M = d-block metal) bond are far less abundant or even non-detectable[4]. This is *different* for compounds bearing halogen substituents at the indium center. The CI mass spectrum of **6** exhibits a base peak at m/z = 372, the isotope pattern agrees with a [$M^{\bullet+}$ – Br] moiety. Thus, cleavage of an In–Br bond now predominates over that of a Co–In bond. Also, for **1b** the molecular ion was not detected. The ion with the highest specific mass (rel. int. 13%) corresponds to a splitting of the Ni–CO bond. Again, the base peak at m/z = 418 results from cleavage of an In–Br bond.

Structure

Compound **1a** was structurally characterized by X-ray single-crystal analysis. Figure 3 shows the molecular structure of **1a** in the solid state. The results confirms the presence of a direct unsupported Ni–In bond in **1a**. The complexes Cp(CO)Ni–In[$(CH_2)_3NMe_2$]$_2$ (**10**)[4] and Cp(PPh_3)Ni–$InBr_2$(O=PPh_3) (**11**)[9a] are the only two other structurally characterized examples of molecular, *non-bridged* Ni–In bonds to date. Some recently reported NiIn complexes contain halide bridges[11].

Figure 3. Molecular structure of (η^5-C_5H_5)(CO)Ni–$InBr_2$-(NC_7H_{13}) (**1a**) in the solid state (PLATON[18] drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability)[a]



[a] Selected bond lengths [pm] and angles [°]: In–Br(1) 255.8(1), In–Br(2) 255.0(1), In–Ni 246.3(1), In–N 227.9(7), Ni–C(1) 171.6(10), O(1)–C(1) 114.1(13), Ni–Cp 172.7; Br(1)–In–Br(2) 106.25(4), Br(1)–In–Ni 113.71(4), Br(1)–In–N 95.5(2), Br(2)–In–Ni 118.3(1), Br(2)–In–N 97.1(2), Ni–In–N 122.4(2), In–Ni–C(1) 89.8(3), In–Ni–Cp 124.0, C(1)–Ni–Cp 145.6; Cp denotes the centroid of the η^5-C_5H_5 ligand.

The structure also confirms the coordination of the base ligand quinuclidine at the indium center. The indium center is tetrahedrally coordinated. The In–N bond length of 227.9(7) pm is within the range of rather strong dative In–N bonds[12]. The coordination geometry at the nickel atom can be described as distorted trigonal-planar, if one counts the cyclopentadienyl ligand as one coordination site. The angle In(1)–Ni(1)–C(1) of 89.8(3)° is considerably *larger* than the corresponding angle of **10**, which amounts to 78.1(1)°[4]. Interestingly, the carbonyl-free derivative **11** exhibits a corresponding angle In–Ni–P of 98.73(6)°[9] which is close to the value of 100.69(7)° measured for Cp(PPh_3)Ni–$GeCl_3$[13] which may be regarded as the closest congener to **1a** reported so far. These angles indirectly show the different electronic situations at the bent d^{10}-[CpNiL$^-$] fragment for ligands L of different π-acceptor capabilities. The charge polarization of **10** should be more pronounced than for **1a** and **11**[4,10]. The most significant difference between **1a** and **10** is the much shorter Ni–In bond of 246.3(1) pm of **1a** compared with the value of 259.8(1) pm of **10**. While the latter distance corresponds well with the sum of the covalent radii of Ni and In (258 ± 5 pm)[4b] and the Ni–In distances in intermetallic alloys (262–265 pm)[7], the Ni–In bond length of **1a** really appears short. However, the indium center of **1a** and **11** [244.65(9) pm] are only four-coordinated and exhibit rather similar Ni–In distances, while **10** contains a five-coordinate indium center, and in the alloys the indium atom is six-coordinate. This may be sufficient to explain the shortened bonds of **1a** and **11**. Recently, a discussion based on Ni(dπ)–σ*(In–N) back-donation was given to rationalize comparably shortened Fe–In and W–In bonds of $[HB(3,5\text{-}Me_2pz)_3]In-Fe(CO)_4$ and $[HB(3,5\text{-}Me_2pz)_3]In-W(CO)_5$ [Fe–In, 246.3(2) ppm; W–In, 278.3(2) pm][14]. With this background, it seems likely to postulate a similar Ni(dπ)–σ*(In–Br) back donation for **1a**. We carried out some standard extended Hückel calculations based on the structure parameters of **1a**[15]. However, no signficant effects were found on the level of the calculations, despite matching orbital symmetry. The somewhat special arrangement of the nickel and indium fragments with a torsion angle C1–Ni–In–Br2 close to 0°, appeared to be a consequence of the minimization of intramolecular steric repulsion.

Conclusions

In this work we presented a simplified method to generate heterodinuclear transition-metal indium complexes. Using a 1:1 mixture of $InBr/InBr_3$ in reactions with transition-metal carbonyl dimers, we obtained the complexes $L(CO)_nM-InBr_2(Do)$. This method can be also applied to other In^{III} species like $BrIn[(CH_2)_3NMe_2]_2$ to get selectively monoalkylated products. It was shown that by use of a dimethylaminoethyl substituted cyclopentadienyl ring an intramolecular Lewis base adduct stabilization from the neighboring transition metal center is possible.

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Experimental

All manipulations were undertaken by using standard Schlenk and glove box techniques under inert gas (purified N_2 or Ar). Solvents were dried under N_2 by standard methods and stored over molecular sieves (4 Å, Merck; residual water <3 ppm H_2O, Karl-Fischer). – IR: Perkin-Elmer 1650 FT-IR. – NMR: JEOL JNM-GX400, JNM-GX270, and Bruker DPX 400 (^{1}H- and ^{13}C-NMR spectra referenced to internal solvent and corrected to TMS). All *J* values reported in Hz (Hertz). All samples for NMR spectra were contained in vacuum sealed NMR tubes. – MS: Finnigan MAT90 (FD spectra); *m/z* values are reported for ^{59}Ni, ^{79}Br, and ^{115}In, normal isotope distribution observed. – Melting points: in sealed capillaries and uncorrected. – The starting compounds $BrIn[(CH_2)_3NMe_2]_2$[16], In^IBr and $[L(CO)_nM]_2$ were prepared as described in the literature. Abbreviations are as follows: Cp = η^5-C_5H_5, Me = CH_3, Ph = C_6H_5. – Elemental analyses were performed at the Microanalytic Laboratory of the Technical University at Munich.

Dibromo[(carbonyl)(η⁵-cyclopentadienyl)nickelo]indium(III)–Quinuclidine Adduct (**1a**) *and the Related Compounds* **1b**, **2**, **3**. – *General Method for the Synthesis:* 2.0 g (6.59 mmol) of $[Cp(CO)Ni]_2$, 1.28 g (6.59 mmol) of finely powdered and freshly sublimed InBr, and 2.34 g (6.59 mmol) of $InBr_3$ were suspended in 40 ml of dioxane and the suspension was heated at refluxe for 4 h. Then the solvent was removed in vacuo and the residue was suspended in 30 ml of toluene. To this suspension a solution of 0.78 g (7 mmol) of quinuclidine in 30 ml of toluene was added dropwise. After stirring for 1 h at ambient temp. the solvent was removed in vacuo and the residue was washed with pentane. Single crystals of **1a** were obtained by slow solvent diffusion (*n*-pentane) using the solvent mixture THF/*n*-pentane (1:1). Yield 62%.

1a: Dark red-brown crystals, m.p. 138 °C. – ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 0.92 [m, 6H, $N(CH_2)_3(C\mathit{H}_2)_3CH$], 1.08 [m, 1H, $N(CH_2)_3(CH_2)_3C\mathit{H}$], 2.92 [m, 6H, $N(C\mathit{H}_2)_3(CH_2)_3CH$], 5.08 (s, 5H, Cp). – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 19.6 [$N(CH_2)_3(CH_2)_3\mathit{C}H$], 24.8 [s, $N(CH_2)_3(\mathit{C}H_2)_3CH$], 47.7 [$N(\mathit{C}H_2)_3(CH_2)_3CH$], 90.9 (Cp), 194.7 (CO). – IR (THF): $\tilde{\nu}$ = 1997 cm^{-1} (vs) [ν(CO)]. – $C_{13}H_{18}InBr_2NNiO$ (537.6): calcd. C 29.04, H 3.37, Br 29.73, In 21.36, N 2.61, Ni 10.92; found C 28.98, H 3.37, Br 30.15, In 20.90, N 2.60, Ni 10.98.

1b: Orange crystals. – ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 1.62 [AA′BB′, 2H, $N(CH_2C\mathit{H}_2]$, 1.87 [AA′BB′, 2H, $N(C\mathit{H}_2CH_2]$, 1.95 [s, 6H, $N(CH_3)_2$], 4.75 [t, $^3J_{H\text{-}H}$ = 2.1 Hz, 2H, C_5H_4], 5.14 [t, $^3J_{H\text{-}H}$ = 2.1 Hz, 2H, C_5H_4]. – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 23.2 [$NCH_2\mathit{C}H_2$], 45.2 [$N(CH_3)_2$], 56.2 [$N\mathit{C}H_2CH_2$], 88.8 (C_5H_4, C_{meta}), 93.4 (C_5H_4, C_{ortho}), 94.1 (C_5H_4, C_{ipso}), 192.0 (CO). – IR (toluene): $\tilde{\nu}$ = 2007 cm^{-1} (vs) [ν(CO)]. – CI-MS; *m/z* (%): 496 (not detected) [M^+], 468 (13) [M^+ – CO], 418 (100) [M^+ – Br], 275 (55) [$InBr_2^+$]. – $C_{10}H_{14}Br_2InNNiO$ (497.6): calcd. C 24.14, H 2.83, Br 32.11, In 23.07, N 2.81, Ni 11.79; found C 24.55, H 2.97, Br 31.70, In 22.90, N 2.83, Ni 11.92.

2: Yellow powder, m.p. 155 °C. – ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 0.88 [m, 6H, $N(CH_2)_3(C\mathit{H}_2)_3(CH$], 1.03 [m, 1H, $N(CH_2)_3(CH_2)_3C\mathit{H}$], 2.88 [m, 6H, $N(C\mathit{H}_2)_3(CH_2)_3CH$]. – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 18.9 [$N(CH_2)_3(CH_2)_3\mathit{C}H$], 24.5 [$N(CH_2)_3\mathit{C}H_2)_3CH$], 48.4 [$N(\mathit{C}H_2)_3(CH_2)_3CH_2)_3CH$], 199.5 (CoCO). – IR (THF): $\tilde{\nu}$ = 2078 cm^{-1} (w), 2060 (w), 1991 (vs) [ν(CO)]. – $C_{11}H_{13}Br_2CoInNO_4$ (556.8): calcd. C 23.73, H 2.35, Br 28.70, Co 10.50, In 20.62, N 2.52; found C 23.41, H 2.31, Br 28.92, Co 10.50, In 20.6, N 2.41.

3: Yellow crystals, m.p. 166 °C. – ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 0.94 [m, 6H, $N(CH_2)_3(C\mathit{H}_2)_3CH$], 1.06 [m, 1H, $N(CH_2)_3(CH_2)_3C\mathit{H}$], 3.09 [m, 6H, $N(C\mathit{H}_2)_3(CH_2)_3CH$], 4.25 (s, 5H, Cp). – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 19.6 [$N(CH_2)_3(CH_2)_3\mathit{C}H$], 24.6 [$N(CH_2)_3(\mathit{C}H_2)_3CH$], 47.9 [s, $N(\mathit{C}H_2)_3(CH_2)_3CH$], 82.2 (Cp), 215.4 (FeCO). – IR (THF): $\tilde{\nu}$ = 1997 cm^{-1} (vs), 1950 (vs) [ν(CO)]. – $C_{14}H_{18}Br_2FeInNO_2$ (562.8): calcd. C 29.88, H 3.22, Br 28.40, Fe 9.93, In 20.40, N 2.49; found C 29.55, H 3.22, Br 28.53, Fe 9.72, In 20.0, N 2.43.

Bis[(carbonyl)(η⁵-cyclopentadienyl)nickelo]indium(III) Bromide (**4**): 0.5 g (1.65 mmol) of $[Cp(CO)Ni]_2$ and 0.381 g (1.96 mmol) of finely powdered and freshly sublimed InBr were suspended in 20 ml of THF and the suspension was stirred for 12 h at ambient temp. The solvent was removed in vacuo and the residue was washed with pentane. The crude product was purified by recrystallization using slow solvent diffusion (*n*-heptane) techniques at ambient temp. with the solvent mixture THF/*n*-heptane (15:40). Yield 80.3%.

4: Dark red-brown powder, m.p. 162 °C (dec.). – ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 5.26 (s, Cp). – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 91.4 (Cp), 192.3 (NiCO). – IR

(THF): ṽ = 1993 cm^{-1} (vs), 1973 (vs) [ν(CO)]. – $C_{12}H_{10}BrInNi_2O_2$ (498.3): calcd. C 28.92, H 2.02, Br 16.04, In 23.04, Ni 23.56; found C 28.31, H 2.25, Br 16.54, In 22.74, Ni 22.38.

[(Bromo)(3-dimethylaminopropyl)indio](tetracarbonyl)-cobalt(–1) (**6**) *and the Related Compounds* **5** *and* **7**: 0.5 g (1.46 mmol) of $Co_2(CO)_8$, 0.285 g (1.46 mmol) of finely powdered and freshly sublimed InBr, and 0.537 g (1.46 mmol) of $BrIn[(CH_2)_3NMe_2]_2$ were suspended in 20 ml of THF and the suspension was stirred for 12 h at ambient temp. After the solvent had been removed in vacuo the product was extracted three times with 20 ml of heptane. The combined extracts were concentrated to about 25 ml and the product was crystallized at –30 °C. Yield 46%. Even higher yields (>75%) were obtained if InBr and $Co_2(CO)_8$ were combined to produce the insertion product and then, after exchange of the solvent THF for toluene, a toluene solution of $BrIn[(CH_2)_3NMe_2]_2$ was added. (The presence of the compounds **5** and **7** in the crude reaction mixtures was detected on the basis of the IR spectra, but analytically pure samples were not obtained.)

6: Light yellow crystals, m.p. 65 °C. – ^1H NMR (400.13 MHz, $[D_8]$toluene, 274 K, *c* = 0.44 mol/l): δ = 0.87 (m, 1 H, $InCH_2$), 1.14 (m, 1H, $InCH_2$), 1.30 (m, 1H, $InCH_2C\mathit{H}_2$), 1.47 (m, 1H, $InCH_2C\mathit{H}_2$), 1.59 (m, 1H, $InCH_2CH_2C\mathit{H}_2NMe_2$), 1.75 (s, 3H, NMe_2), 1.77 (m, 1H, $InCH_2CH_2C\mathit{H}_2NMe_2$), 1.88 (s, NMe_2, dimer), 2.11 (s, 3H, NMe_2). – $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$toluene, 200 K, *c* = 2.15 mol/l): δ = 7.1 ($InCH_2$, dimer **6a**), 12.8 (s, $InCH_2$, monomer **6**), ($InCH_2CH_2$, dimer **6a**, not found), 18.3 (In CH_2CH_2, monomer **6**), 38.9 (NMe_2, monomer **6**), 40.2 (NMe_2, dimer **6a**), 42.3 (NMe_2, monomer **6**), 56.0 (CH_2N, dimer **6a**), 56.7 (CH_2N, monomer **6**). – IR (*n*-heptane): ṽ = 2079 cm^{-1} (s), 2064 (w), 2018 (s), 1990 (vs), 1971 (vs) [ν(CO)]. – MS; *m/z* (%): 452 (not detected) [M^+], 423 (3) [M^+ – CO], 372 (100) [M^+ – Br], 344 (3) [M^+ – Br – CO], 280 (23) [M^+ – $(CO)_4Co$]. – $C_9H_{12}BrCoInNO_4$ (451.9): calcd. C 23.92, H 2.68, Br 17.68, Co 13.04, In 25.41, N 3.10; found C 23.85, H 2.61, Br 17.79, Co 13.10, In 25.2, N 3.13.

[{[3-(Dimethylamino)propyl}bis(tetracarbonylcobalto)]indium(III) (**8**) *and the Related [(3-Dimethylaminopropyl)(pentacarbonylmangano)(tetracarbonylcobalto)indium(III)* (**9**). – *General Method of the Synthesis:* 0.46 g (1.07 mmol) of **6** was dissolved in 20 ml of THF at –78 °C. At this temperature a solution of 0.273 g (1.3 mmol) of $KCo(CO)_4$ in 20 ml of THF at –78 °C was quickly added in one portion with vigorous stirring. The reaction mixture was allowed to warm up to ambient temp. within 10 min. After stirring of the reaction mixture at ambient temp. for 0.5 h, the solvent was removed in vacuo. The residue was extracted three times with 20 ml of *n*-pentane each. The combined solutions were concentrated to a volume of 20 ml. Slow cooling of the solution to –30 °C afforded yellow crystals of **8**. Yield 76%.

8: Light yellow crystals, m.p. 67 °C. – ^1H NMR (399.78 MHz, $[D_8]$toluene, 25 °C): δ = 1.22 (t, 2H, 7.33 Hz, $InCH_2$), 1.59 (q, 2H, 6.22 Hz, $InCH_2C\mathit{H}_2$), 1.89 (t, 2H, $InCH_2CH_2C\mathit{H}_2$), 1.91 (s, 6H, NMe_2). – $^{13}C\{^1H\}$ NMR (100.5 MHz, $[D_8]$toluene, 25 °C): δ = 21.1 ($InCH_2$), 24.3 ($InCH_2CH_2$), 46.5 (NMe_2), 63.2 (CH_2N). – IR (*n*-pentane): ṽ = 2080 cm^{-1} (w), 2064 (s), 2017 (w), 2006 (s), 1992 (vs), 1978 (vs), 1959 (w) [ν(CO)]. – $C_{13}H_{12}Co_2InNO_8$ (542.9): calcd. C 28.76, H 2.23, Co 21.71, In 21.15, N 2.58; found C 28.25, H 2.23, Co 21.6, In 21.0, N 2.58.

9: Light yellow powder, m.p. 70 °C. – ^1H NMR (399.78 MHz, $[D_8]$toluene, 25 °C): δ = 1.22 (m, 2H, $InCH_2$), 1.59 (m, 1H, $InCH_2C\mathit{H}_2$), 1.80 (m, 1H, $InCH_2C\mathit{H}_2$), 1.97 (m, 4H, $InCH_2CH_2C\mathit{H}_2N\mathit{Me}_2$), 2.02 (s, 3H, NMe_2), 2.10 (m, 1H, $InCH_2CH_2C\mathit{H}_2NMe_2$). – $^{13}C\{^1H\}$ NMR (100.5 MHz, $[D_8]$toluene, 25 °C): δ = 22.8 ($InCH_2$), 25.0 ($InCH_2CH_2$), 46.9 (NMe_2), 47.8 (NMe_2), 64.4 (CH_2N), 203 (CO), 217 (CO). – IR (*n*-pentane): ṽ = 2084 cm^{-1} (w), 2061 (s), 2004 (s), 1984 (vs), 1965 (s), 1952 (w) [ν(CO)]. – $C_{14}H_{12}CoInMnNO_9$ (566.9): calcd. C 29.66, H 2.13, Co 10.39, In 20.25, Mn 9.69, N 2.47; found C 29.14, H 2.04, Co 10.3, In 20.4, Mn 9.72, N 2.37.

Reaction of Dibromo[di(carbonyl)(η⁵-cyclopentadienyl)iron]indium(III)–Quinuclidine Adduct (**3**) *with Sodium Iodide. – Synthesis of* **3a**: A solution of 0.3 g (0.53 mmol) of **3** and 0.8 g (5.3 mmol) of dried NaI in 30 ml of THF was stirred 3 h at ambient temp. After the solvent had been removed in vacuo the product was extracted three times with toluene. The combined toluene solutions were concentrated to about 20 ml and the product was crystallized at –30 °C; yellow powder.

3a: ^1H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 0.92 [m, 6H, $N(CH_2)_3(C\mathit{H}_2)_3CH$], 1.04 [m, 1H, $N(CH_2)_3(CH_2)_3C\mathit{H}$], 3.07 [m, 6H, $N(C\mathit{H}_2)_3(CH_2)_3CH$], 4.23 (s, 5H, Cp). – $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 19.5 [$N(CH_2)_3(CH_2)_3\mathit{C}H$], 24.3 [s, $N(CH_2)_3(\mathit{C}H_2)_3CH$], 47.9 [$N(\mathit{C}H_2)_3(CH_2)_3CH_2)_3CH$], 83.1 (Cp). – IR (THF): ṽ = 1983 cm^{-1} (vs), 1935 (vs) [ν(CO)]. – $C_{14}H_{18}FeI_2$-$InNO_2$ (656.8): calcd. C 24.77, H 2.83, N 1.85; found C 24.60, H 2.76, N 2.13.

Reaction of Dibromo[(carbonyl)(η⁵-cyclopentadienyl)-nickelo]indium(III)–Quinuclidine Adduct (**1a**) *with Tetraphenylphosphonium Bromide and Quinuclidine Hydrobromide. – Synthesis of* **1c** *and* **1d**: A solution of 0.125 g (0.23 mmol) of **1a** and 0.044 g (0.23 mmol) of quinuclidine hydrobromide in 10 ml of THF was stirred 1 h at ambient temp. {**1c**: IR (THF): ṽ = 1994 cm^{-1} (vs), 1967 (sh) [ν(CO)]}. A solution of 0.153 g (0.29 mmol) of **1a** and 0.120 g (0.29 mmol) of tetraphenylphosphonium bromide in 10 ml of THF was stirred for 1 h at ambient temp. {**1d**: IR (THF): ṽ = 1988 cm^{-1} (vs), 1964 (sh) [ν(CO)]}. The structure of **1c** was proven by X-ray single crystal diffraction (see below).

X-ray Structure Determination of $(\eta^5\text{-}C_5H_5(CO)Ni\text{–}InBr_2(NC_7H_{13})$ (**1a**) *and* $[(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}InBr_3][HNC_7H_{13}]$ (**1c**): Crystals of the compound **1a** were grown by slow solvent diffusion techniques from *n*-pentane/tetrahydrofurane mixtures at ambient temp. over several days. According to surprisingly similar solubility properties, crystals of **1a** as well as significant amount of $[(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}InBr_3][HNC_7H_{13}]$ (**1c**, an impurity presumably formed by hydrolysis of **1a**) were present in the sample. **1c** was then independently synthesized (see above). The two typs of crystals had the same color (red-brown) but could be separated manually by using a microscope. Crystals of **1a** are orthorhombic, crystals of **1c** monoclinic. An X-ray powder diffractogram of a finely ground sample of crystals of **1a** was recorded to verify quantitative separation. The diffractograms were obtained from thin films of the crystal powder in asymmetric transmission (1° < Θ < 30°) with a HUBER Guinier 642 camera by using the system software Guinier 600 5.18 by Michael Nippus, Huber Diffraktionstechnik GmbH, Rimsting, Germany. The data analysis was performed by using the programs "PARAM" by M. Birkhahn, E. Herdtweck, University of Marburg (1982) and TU Munich (1985), and "POWDMULT 2.2" by E. Wu, School of Physical Sciences Bedford Park, S. A. 5042, Australia. All peaks could be indexed on the basis of the single-crystal data by use of those programs. A suitable single crystal of **1a** was then selected and the preliminary examination and the final data collection for **1a** were carried out with an Enraf-Nonius CAD4 diffractometer. Final cell constants were obtained by least-squares refinements of 25 automatically centered high-angle reflections 39.7 < 2Θ < 46.2° with the programs "SET4/CELDIM"[18] and were in perfect agreement with the values obtained from the powder diffraction studies. During data collection orientation control reflections were monitored every

200th, and the intensity of three reflections were checked every 3600 s. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 3. The reflection data were corrected for Lorentz and polarization factors. During 93.2 h of exposure the three control reflections lost 34.5% of their intensity. Corrections for decay, absorption empirical, and extinction were applied. Anisotropic thermal parameters were applied for all non-hydrogen atoms. The hydrogen positions were placed in ideal geometry (riding model) and were included into the structure refinement with isotropic temperature factors but not refined. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w (F_o^2 - F_c^2)^2$. All calculations were performed with a Micro VAX 3100 computer with the STRUX-V system[18] including the programs SHELXL-93, PLATON, PLUTON, SDP, and SHELXS-86. The structure was solved by direct methods and subsequent difference Fourier maps. The refinement was stopped at a shift/err < 0.001, and final difference Fourier maps showed no significant features. The Flack-parameter of −0.01(2) revealed the correct choice of the enantiomere. An attempt was made to model the disorder of the cyclopentadienyl ring ligand (indicated by the quite large thermal vibration factors for C-3, C-5, and C-6). However, they did not lead to an improvement of the overall quality of the structure refinement. Supplementary material including full crystallographic and experimental data, hydrogen positional parameters, thermal parameters, interatomic distances, and bond angles are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404459, the names of the authors, and the journal citation.

A single crystal of **1c** was also selected, and the reflection data were collected as above. But due to a major disorder of the quinuclidinium ion and the Cp ligand, we did not discuss the structure properties. These problems cannot result from twinning as proven by Buerger and de Joug-Bouman precession photographs but probably arose from poor quality of the selected crystals. **1c** crystallizes in the monoclinic space group $P2_1$ (No. 4). The cell constants are as follows: a = 762.4(2), b = 985.4(2), c = 1274.7(2) pm, β = 91.35(2)°, V = 957 · 10⁶(1) pm³, ρ = 2.146 g cm^{-3}. For further details contact the authors E. H. and A. F.

Table 3. Crystallographic and data collection parameters for **1a**

Formula	$C_{13}H_{18}Br_2InNNiO$ (**1a**)
Crystal size, mm^3	0.41 × 0.41 × 0.51
M [g mol^{-1}]	537.61
Space group	$P2_12_12_1$ (No. 19)
T [K]	296(1)
λ [pm]	71.073
a [pm]	924.1(1), 925.9(3)[a]
b [pm]	1334.2(2), 1335.0(4)[a]
c [pm]	1342.4(2), 1341.7(5)[a]
V [10^6 · pm^3]	1655.1(4), 1659(3)[a]
Z	4
μ [cm^{-1}]	73.5
Measurement range	$1.0 < \Theta < 26.0$
Scan type	ω-scan
$\rho_{calcd.}$ [g · cm^{-3}]	2.158
No. of unique reflections	2965
No. of refined reflections	2965
$R1$[b]	0.0451
$wR2$[c]	0.1096
GOF	1.095

[a] Values obtained from the powder diffraction studies. 37 reflections ($9.34 < 2\Theta < 46.62$) were used in refinements. – [b] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0658 \cdot P)^2 + 3.9155 \cdot P$ [$P = (F_o^2 + 2 \cdot F_c^2)/3$].

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