Metal Complexes of Biologically Important Ligands, XCIV[◇]

Hexanuclear Isocyanide and Carbene Metal Complexes from Neomycin B☆

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From the amino glycoside neomycin B, the acetate-protected hexaisocyanide **4** has been prepared. **4** forms the hexanuclear complexes [(**4**)$(AuCl)_6$] (**5**), {(**4**)$[Cr(CO)_5]_6$}, {(**4**)$[MCl_2(\eta^5\text{-}C_5Me_5)]_6$} (M = Rh, Ir), {(**4**)$[RuCl_2(p\text{-cymene})]_6$}, {(**4**)$[MCl_2(PR_3)]_6$} (M = Pd, Pt), and **4**{(**4**)$[PdCl(C_6H_4CH_2NMe_2)]_6$}. The hexaisocyanohexagold(I) complex **5** reacts with H_2NtBu and $PhNH_2$ to give the corresponding carbene complexes. The compounds have been characterized by IR, ^{13}C- and ^{31}P-NMR spectroscopy, and (partially) by FAB-MS data.

Recently, organometallic complexes in which carbohydrate derivatives are bound to the metal atom through isocyanide or carbene functions have been reported by Aumann[2], Fischer[3], in a series of papers by Dötz[4] and first by our group[5]. Neomycin B is an amino glycoside and we became interested in using this antibiotic[6] or its derivatives as polyfunctional ligands[7]. We report herein on the synthesis of hexadeamino-hexaisocyano-neomycin B and of metal complexes thereof.

Synthesis of the Ligand and the Complexes

In close analogy to a procedure reported by Barton et al.[8] for the synthesis of acetyl-protected 2-deoxy-2-isocyano-β-D-glucose and the diglycoside tetradeamino-tetraisocyano-neamine, the antibiotic neomycin B (**1**) was treated with *p*-nitrophenyl formate in DMF/H_2O to give the fully *N*-formylated compound **2**. Peracetylation of **2** afforded the heptaacetate **3**, from which the hexaisocyanide **4** was obtained by treatment with phosphorus oxychloride and triethylamine.

Reaction of the hexaisocyanide **4** with Me_2SAuCl, $Cr(CO)_5THF$ and the chloro-bridged complexes $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ (M = Rh, Ir), $[(p\text{-cymene})RuCl_2]_2$, $[(R_3P)_4MCl_2]_2$ (M = Pd, Pt), $[(\pi\text{-allyl})PdCl]_2$ and $[ClPdC_6H_4CH_2NMe_2]_2$ gave the hexanuclear isocyanide complexes **5**–**14**. In contrast to the gold(I) complex **5**, the other compounds **6**–**14** are – owing to the presence of lipophilic PR_3 or C_5Me_5 ligands – soluble in organic solvents and some of them could be purified by column chromatography. As has been reported for a series of monomeric isocyanogold(I) complexes[5][9], the reaction of **5** with $tBuNH_2$ and $PhNH_2$ yields the hexacarbene complexes **15** and **16**, respectively.

Characterization of the Complexes

In the IR spectra of the complexes **5**–**14** (Table 1), only one ν(CN) absorption is observed, which proves complete coordination of all six isocyanide functions. In comparison to the free ligand, a shift of 70–100 cm^{-1} to higher ν(CN) absorptions is apparent for **5**, **10**–**14**, indicating metal–carbon σ-bonding, whereas in **6**–**9** some metal–CN π-bonding may occur. The carbene complexes **15** and **16** show the disappearance of the ν(C≡N) band and characteristic ν(NH) and ν(NCN) absorptions.

The ^{13}C-NMR spectra of complexes **7**, **8** and **11** (Table 2) exhibit an upfield shift of all six isocyanide resonances compared to the free ligand, which again proves coordination of all of the isocyanide ligands. The different stereochemical environments for the organometallic moieties [e. g. $(\eta^5\text{-}C_5Me_5)M$ (M = Rh, Ir)] leads to several C resonances for the other organic ligands. The C-carbene resonance of **16** appears at $\delta \approx 190$, a region which is characteristic of (aminocarbene)gold(I) complexes[5][9].

In the ^{31}P-NMR spectra of the phosphane complexes (Table 3), the appearance of only one signal indicates the non-existence of *cis*/*trans* isomers.

FAB mass spectra (Table 4) could be obtained from **7** and **14**. They show $[M^+ - Cl]$ as ions with the highest mass and successive loss of the organometallic moietics.

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[◇] Part XCIII: Ref.[1].

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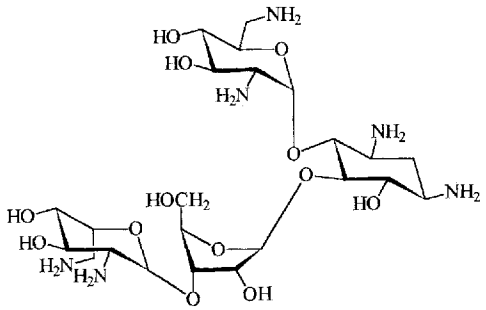
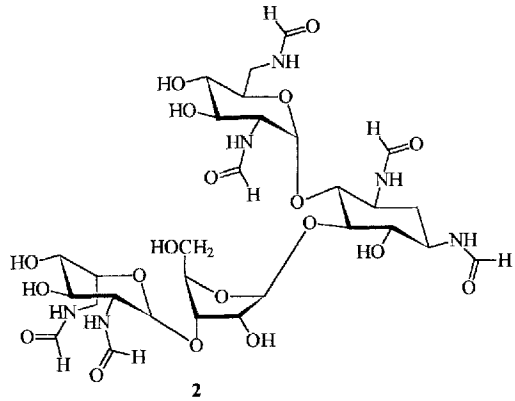


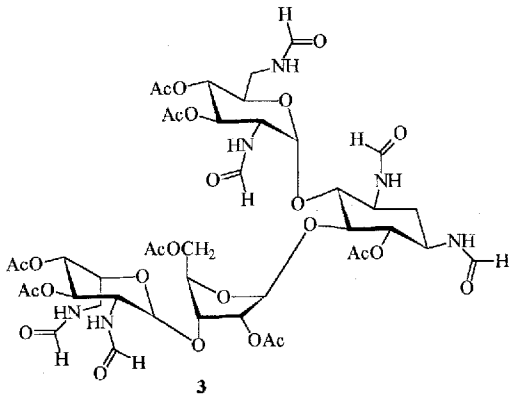
Neomycin B (**1**)

HCO_2-*p*-$C_6H_4NO_2$
DMF/H_2O



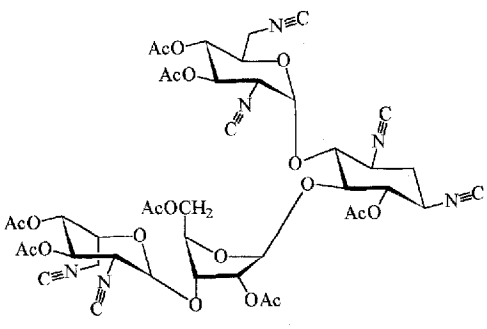
2

Ac_2O/
Pyridine

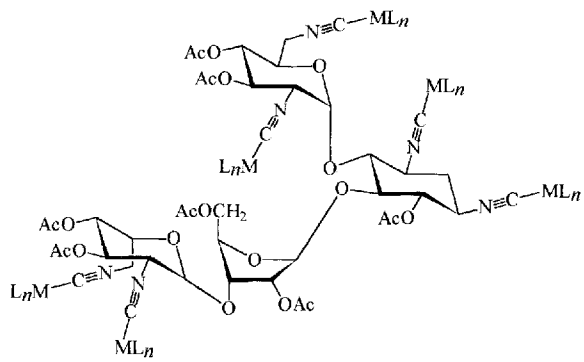


3

$POCl_3$/NEt_3
-40°C

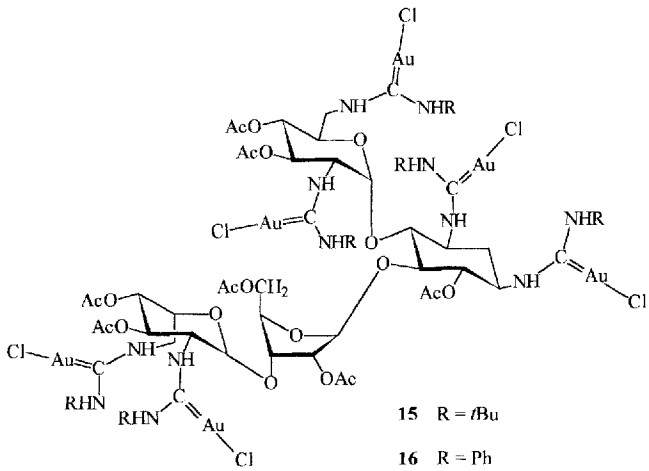


4



	5	6	7	8	9
ML_n	AuCl	$Cr(CO)_5$	$RhCl_2(\eta^5\text{-}C_5Me_5)$	$IrCl_2(\eta^5\text{-}C_5Me_5)$	$RuCl_2$(*p*-cymene)

	10	11	12	13	14
ML_n	$PdCl_2(PEt_3)$	$PdCl_2(PnBu_3)$	$PtCl_2(PnBu_3)$	PdCl(π-Allyl)	$PdCl(C_6H_4CH_2NMe_2)$



15 R = *t*Bu

16 R = Ph

Table 1. Characteristic IR data [cm^{-1}] of **4**–**16**

	ν(NC) or ν(N–C–N)	ν(M–Cl)	others
4	2153 vs		1755 vs, br [ν(CO)]
5	2251 vs	351 m	1753 vs, br [ν(CO)]
6	2165 s		1752 s [ν(CO)]
			2066 s
			1937 vs, br [ν(MCO)]
7	2202 vs		1751 vs [ν(CO)]
8	2187 vs, br	295 m	1752 s [ν(CO)]
9	2187 vs, br	282 m	1749 s [ν(CO)]
10	2227 vs	320 w, sh	1752 s [ν(CO)]
11	2226 vs	316 w, sh	1755 s [ν(CO)]
12	2223 vs, br	342 m	1755 s [ν(CO)]
		332 w, sh	
13	2207 vs, br	378 vw, sh	1752 vs, br [ν(CO)]
14	2218 vs	360 w	1753 vs [ν(CO)]
15	1563 s, br	324 w	1747 s [ν(CO)]
			3229 m, br
			3066 m, br [ν(NH)]
16	1599 m	326 m	1746 s, br [ν(CO)]
	1555 vs, br		3273 s, br
	1496 s		3061 m, br [ν(NH)]

Table 2. Selected ^{13}C-NMR data (100.53 MHz, $CDCl_3$) of **4**, **7**, **8**, **11**, **16**[a]

	CN	$COCH_3$	$COCH_3$	ring C	others
4	161.98;	170.82;	23.39;	107.27; 98.44; 95.72;	
	161.40;	170.32;	21.09;	94.19; 81.44; 78.86;	
	160.83;	169.80;	20.84;	74.99; 74.52; 73.34;	
	160.79;	169.70;	20.77;	71.95; 69.53; 68.16;	
	160.27;	169.39;	20.65;	67.76; 67.33; 64.97;	
	159.78	169.32;	20.58;	62.09; 55.29; 51.45;	
		168.24	20.53	50.36; 42.15; 41.70; 33.30; 32.95	
7	130.77;	170.58;	21.53;	113.66; 107.24; 96.86;	C_5Me_5:
	128.69;	170.51;	21.45;	93.94; 80.68; 78.05;	100.20; 100.13; 100.05;
	128.36;	170.20;	21.05;	75.23; 74.79; 73.63;	99.99; 99.93; 99.69
	127.34;	170.15;	20.92;	71.35; 71.15; 69.37;	$C_5\mathit{Me}_5$:
	126.86;	170.12;	20.89;	68.46; 67.83; 67.58;	9.82; 9.52; 9.49; 9.37;
	126.04	169.20;	20.71;	66.33; 65.70; 53.71;	9.29; 9.26
		168.05	20.66	52.86; 46.73; 43.49; 33.63; 31.64	
8	127.31;	170.05;	21.05;	106.97; 99.71; 96.89;	C_5Me_5:
	126.30;	169.96;	21.01;	85.72; 80.64; 74.47;	94.11; 94.07; 94.01;
	125.96;	169.88;	20.55;	73.54; 69.03; 68.27;	93.86; 93.68; 93.37
	125.00;	169.83;	20.50;	67.21; 66.18; 63.51;	$C_5\mathit{Me}_5$:
	124.89;	169.61;	20.44;	58.04; 54.12; 53.50;	9.08; 9.02; 8.88; 8.78;
	122.40	168.86;	20.34;	53.05; 52.37; 46.31;	8.74; 8.67
		167.63	20.27	42.96; 34.16; 31.42; 30.50; 28.84	
11	130.82;	170.55;			
	130.30;	170.15;			
	129.74;	169.92;			
	128.63;	169.52;			
	128.23;	169.18;			
	126.66	168.89;			
		168.65			
16	193.28;	171.56;			
	190.89;	171.24;			
	190.69;	171.20;			
	188.55;	171.17;			
	187.95;	170.51;			
	187.77	169.59;			
		169.20			

[a] The resonances of the other complexes are very similar to that shown in Table 2.

Table 3. ^{31}P-NMR data (36.23 MHz, H_3PO_4 as standard, $CDCl_3$) of **10**–**12**

	δ	$^1J(^{31}P,^{195}Pt)$
10	44.96; 44.49; 44.15; 43.48; 43.14; 42.54	
11	35.40; 35.07; 34.66; 34.33; 34.06; 33.65	
12	8.65; 8.41; 8.04; 7.84; 7.57; 7.34	3140 Hz

Table 4. Selected FAB-MS data of 7 and **14**

	Fragment ion	*m/z* (%)
7	$[M-Cl]^+$	2788.0 (10)
	$[M-Cl-(C_5Me_5RhCl_2)]^+$	2479.2 (5)
	$[M-2Cl-(C_5Me_5RhCl_2)]^+$	2444.2 (5)
	$[M-Cl-2(C_5Me_5RhCl_2)]^+$	2169.8 (20)
	$[M-2Cl-2(C_5Me_5RhCl_2)]^+$	2134.2 (15)
	$[M-Cl-3(C_5Me_5RhCl_2)]^+$	1859.1 (40)
	$[M-Cl-4(C_5Me_5RhCl_2)]^+$	1552.2 (40)
	$[M-Cl-5(C_5Me_5RhCl_2)]^+$	1243.4 (100)
14	$[M-Cl]^+$	2590.8 (100)
	$[M-Cl-(PdC_9H_{12}NCl)]^+$	2311.5 (50)
	$[M-Cl-2(PdC_9H_{12}NCl)]^+$	2038.5 (50)
	$[M-Cl-3(PdC_9H_{12}NCl)]^+$	1760.9 (40)
	$[M-Cl-5(PdC_9H_{12}NCl)]^+$	1209.6 (10)

Experimental Section

Neomycin sulfate was purchased from Sigma. The complexes Me_2SAuCl[10], $Cr(CO)_5THF$[11], $[(\eta^5\text{-}C_5H_5)MCl_2]_2$ (M = Rh, Ir)[12], [(*p*-cymene)$RuCl_2]_2$[13], $[(R_3P)MCl_2]_2$ (M = Pd, Pt)[14], $[(\eta^3\text{-allyl})PdCl]_2$[15] and $[ClPdC_6H_4CH_2NMe_2]_2$[16] were prepared as described in the literature. – IR: Perkin-Elmer 841, Nicolet 520. – NMR: JEOL FX 90, EX 400. – MS: Finnigan MAT 90. – CHN analyses: Heraeus VT.

Hexa-N-formyl-neomycin B (**2**): To a solution of 12.4 g (13.7 mmol) of neomycin · 3 H_2SO_4 in 80 ml of water, 12.9 g of $Ba(OH)_2 \cdot 8\ H_2O$ was added in portions. After stirring, the precipitate of $BaSO_4$ was filtered off and the filtrate was treated with 80 ml of DMF and 20.7 g of *p*-nitrophenyl formate. The mixture was stirred for 36 h at room temp. The solvent was then removed in vacuo affording a colorless oil. On addition of 200 ml of diethyl ether, **2** was deposited as a colorless solid, which was stirred for 2 h in diethyl ether, separated by filtration and washed three times. Colorless powder; quantitative yield.

Hepta-O-acetyl-hexa-N-formyl-neomycin B (**3**): Compound **2** was dried in vacuo and then suspended in a mixture of 135 ml of acetic anhydride and 240 ml of dry pyridine. The mixture was stirred for 2 d at room temp., resulting in an almost clear solution. After filtration the solvent and reagents were removed in vacuo. Residual traces of acetic anhydride and pyridine were completely removed from the colorless residue by repeated azeotropic distillation with dry toluene. The product was dissolved in chloroform, precipitated by slow addition of 100 ml of hexane, and dried in vacuo over P_2O_5 at 60 °C. Colorless powder, yield 9.11 g (58%), m. p. 153 °C. – IR (Nujol): $\tilde{\nu}$ = 3430 (NH), 1752 (OAc), 1692 cm^{-1} (CO).

Hepta-O-acetyl-hexadeamino-hexaisocyano-neomycin B (**4**): To a stirred solution of 9.11 g (8.4 mmol) of **3** in 200 ml of dichloromethane at −40 °C (2-propanol/CO_2), 35.7 ml of triethylamine and 9.3 ml of $POCl_3$ were added dropwise. The mixture was then allowed to warm to room temp. and stirred for 2 d. After cooling to 0 °C, phosphorus oxychloride was hydrolysed by the addition of an ice-cold saturated aqueous solution of $NaHCO_3$ (500 ml). The organic layer was separated and the aqueous phase was extracted with three 100-ml portions of dichloromethane. The combined organic extracts were dried with Na_2SO_4 and the solvent was removed in vacuo. The brown, oily residue was purified by column chromatography on dry Kieselgel 60 (Merck) using $CHCl_3/CH_3OH$ (9:1) as the eluent. The resulting yellow solution was concentrated and further purified on dry Kieselgel 60 with toluene/THF (4:1) as the eluent. The main colorless fraction, eluted first, was collected and the solvent was removed in vacuo. From the residual colorless oil, a colorless precipitate was obtained by addition of 200 ml of diethyl ether. The product **4** was recrystallized several times from diethyl ether. Colorless powder, yield 4.59 g (34%, based on neomycin B), m. p. 138 °C. – $C_{43}H_{48}N_6O_{20} \cdot H_2O$ (986.9): calcd. C 52.33, H 5.11, N 8.52; found C 52.00, H 5.20, N 8.37.

5: To a solution of 200 mg (0.203 mmol) of **4** in 5 ml of dry dichloromethane in a Schlenk tube, 359 mg (1.22 mmol) of Me_2SAuCl in 5 ml of dichloromethane was added. From the white suspension thus obtained, the solid was separated by centrifugation, washed three times with dichloromethane and dried at 50 °C in vacuo. Colorless powder, yield 298 mg (62%), m. p. 185 °C (dec.). – $C_{43}H_{48}Au_6Cl_6N_6O_{20}$ (2363.4): calcd. C 21.85, H 2.05, N 3.56; found C 21.86, H 2.54, N 3.47.

6: A solution of 245 mg (1.114 mmol) of $Cr(CO)_6$ in 50 ml of THF was irradiated for 3 h. To the clear yellow solution, 183 mg (0.186 mmol) of **4** was added and the mixture was stirred for 24 h.

The solvent was then removed in vacuo from the almost colorless solution, the residue was washed several times with pentane and dried at 50 °C over P_2O_5 in vacuo. Colorless powder, yield 256 mg (65%), m. p. 192 °C (dec.). – $C_{73}H_{48}Cr_6N_6O_5$ (2121.2): calcd. C 41.34, H 2.28, N 3.96; found C 41.46, H 2.80, N 4.39.

General Procedure for Complexes **7**–**9**: To a solution of 50 mg (0.051 mmol) of **4** in 50 ml of dichloromethane, a solution of 0.153 mmol of the chloro-bridged complex $[(\eta^5\text{-}C_5H_5)MCl_2]_2$ (M = Rh, Ir) or $[(p\text{-cymene})RuCl_2]_2$ in 3 ml of dichloromethane was added and the mixture was stirred at room temp. After 2 h, the solvent was removed in vacuo and the residue was purified by column chromatography on Kieselgel 60 (Merck) using acetone as the eluent. The crystalline product was obtained by concentration of the eluate and layering with 20 ml of diethyl ether.

7: Orange-red crystals, yield 147 mg (95%), m. p. 180 °C (dec.). – $C_{103}H_{138}Cl_{12}N_6O_{20}Rh_6$ (3035.4)·2.5 CH_2Cl_2: calcd. C 41.75, H 4.75, N 2.77; found C 41.75, H 5.10, N 2.67.

8: Yellow-orange crystals, yield 164 mg (90%), m. p. 180 °C (dec.). – $C_{103}H_{138}Cl_{12}Ir_6N_6O_{20}$ (3571.3)·2.5 CH_2Cl_2: calcd. C 35.48, H 4.04, N 2.35; found C 34.95, H 4.32, N 2.34.

9: Wine-red crystals, yield 138 mg (90%), m. p. 145 °C (dec.). – $C_{103}H_{132}Cl_{12}N_6O_{20}Ru_6$ (3018.4)·2.5 CH_2Cl_2: calcd. C 41.98, H 4.58, N 2.78; found C 42.48, H 4.59, N 2.76.

General Procedure for Complexes **10**–**14**: A solution of 60 mg (0.061 mol) of **4** in 5 ml of dichloromethane was added dropwise to a solution of the chloro-bridged palladium or platinum complex $[(R_3P)MCl_2]_2$ (M = Pd, Pt), $[(\eta^3\text{-allyl})PdCl]_2$ or $[ClPdC_6H_4CH_2NMe_2]_2$ in 3 ml of dichloromethane, resulting in a bright coloration. After stirring for 1 h at room temp., the solvent was removed in vacuo. The light-yellow residue was washed twice with diethyl ether and dried in vacuo at 50 °C over P_2O_5.

10: Light-yellow powder, yield 158 mg (95%), m. p. 180 °C (dec.). – $C_{79}H_{138}Cl_{12}N_6O_{20}P_6Pd_6$ (2741.8): calcd. C 34.61, H 5.07, N 3.07; found C 34.08, H 5.15, N 3.20.

11: Yellow powder, yield 178 mg (90%), m. p. 180 °C (dec.). – $C_{115}H_{210}Cl_{12}N_6O_{20}P_6Pd_6$ (3246.7): calcd. C 42.54, H 6.52, N 2.59; found C 42.10, H 6.52, N 2.72.

12: Yellow powder, yield 219 mg (95%), m. p. 160 °C (dec.). – $C_{115}H_{210}Cl_{12}N_6O_{20}P_6Pt_6$ (3778.7): calcd. C 36.55, H 5.60, N 2.22; found C 36.24, H 5.72, N 2.33.

13: Light-yellow powder, yield 120 mg (95%), m. p. 180 °C (dec.). – $C_{61}H_{78}Cl_6N_6O_{20}Pd_6$ (2066.6): calcd. C 35.45, H 3.80, N 4.07; found C 34.90, H 3.95, N 3.98.

14: Yellow powder, yield 149 mg (90%), m. p. 180 °C (dec.). – $C_{97}H_{120}Cl_6N_{12}O_{20}Pd_6$ (2710.3): calcd. C 43.3, H 4.54, N 6.20; found C 43.53, H 4.83, N 6.06.

15: To 120 mg (0.051 mmol) of **5** was added 2 ml (20 mmol) of *tert*-butylamine and the light-yellow suspension was stirred for 15 h at room temp. The excess amine was then removed in vacuo and the residue was dissolved in 10 ml of dichloromethane. Undissolved material was centrifuged off and then the solvent was removed from the solution in vacuo. The residue was washed three times with diethyl ether and dried in vacuo over P_2O_5 at 60 °C. – Light-yellow powder, yield 121 mg (75%), m. p. 125 °C (dec.). – $C_{67}H_{114}Au_6Cl_6N_{12}O_{20}$ (3167.9)·5 tBuNH$_2$: calcd. C 32.99, H 5.38, N 7.52; found C 33.03, H 5.36, N 7.47.

16: A solution of 200 mg (0.085 mmol) of **5** in 3 ml of aniline was stirred for 15 min at room temp. From the clear, light-yellow solution the excess aniline was removed in vacuo and the white product was precipitated with 30 ml of diethyl ether, centrifuged off, washed twice with diethyl ether and once with 50 ml of dichloromethane, and dissolved in 5 ml of acetone. After separation of the solid material by centrifugation, the solvent was evaporated in vacuo. The residue was dried in vacuo at 60 °C over P_2O_5. – Light-yellow powder, yield 161 mg (65%), m. p. 145 °C (dec.). – $C_{79}H_{90}Au_6Cl_6N_{12}O_{20}$ (2922.2): calcd. C 32.47, H 3.10, N 5.75; found C 32.37, H 3.55, N 5.75.

☆ Dedicated to Professor *Armin Weiß* on the occasion of his 70th birthday.

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