Supplementary Information

All work was carried out excluding humidity and air in an atmosphere of dried and purified nitrogen (Westfalen AG) using vacuum glass lines or a glove box (MBraun). Solvents were dried over activated alumina. All reaction vessels were made of borosilicate glass and dried before use.

Preparation of $[(Ph_3P)_2AgReO_4]_2$

The compound was obtained best from $AgReO_4$ and PPh_3 in a ratio of 1:2 in boiling acetonitrile after 16 hours as a rose colored product in 92 % yield. Redissolving in acetonitrile and slow evaporation led to the formation of colorless, light and air stable single crystals.

Preparation of $[Ag(PPh_3)_4][ReO_4]$

Starting at $AgReO_4$: PPh_3 ratios of 1 : 3, $[Ag(PPh_3)_4][ReO_4]$ is always obtained. The exact 1:4 ratio leads to the formation of phase pure product after 3 hours of reaction time in a benzene/acetonitrile 2/1 mixture at room temperature. After workup, the colorless precipitate was dried in vacuo, yielding the light and air stable compound (89 %). The compound is also obtained without Schlenk techniques. In order to obtain single crystals, the compound was recrystallized from benzene/acetonitrile under slow cooling (3 °C/min) from 80 °C to room temperature.

ATR-IR spectra (4000 – 600 cm^{-1}, Figg. S1, S2), NMR and chemical analysis data

a) $[Ag(PPh_3)_4][ReO_4]$:

^{31}P-NMR: +10,8 ppm (s) for coordinated PPh_3 (free PPh_3 is observed at -4.7 ppm).
Elem. anal. (% found / % calc.): C 61.5, 61.45, H 4.3, 4.3, P 9.7, 8.8

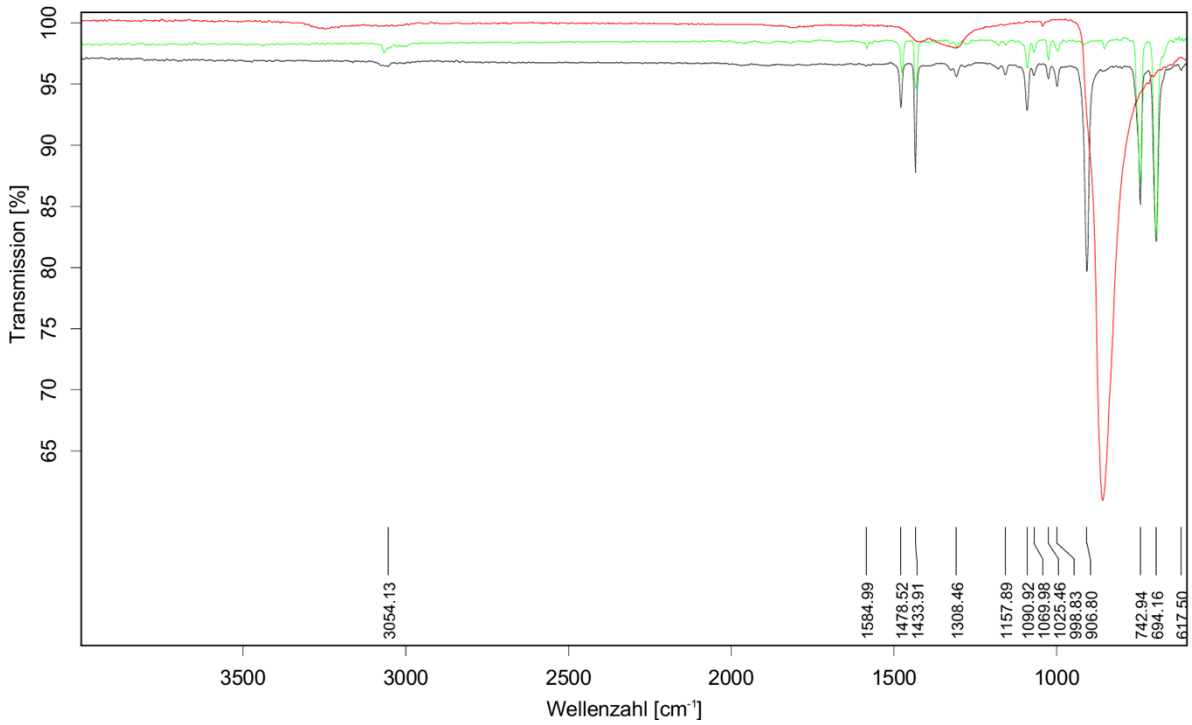

Fig. S1 IR spectra of $[Ag(PPh_3)_4][ReO_4]$ (black), PPh_3 (green) and $AgReO_4$ (red)

b) $[(Ph_3P)_2AgReO_4]_2$

^{31}P-NMR: + 11.3 ppm (s)
Elem. anal. (% found / % calc.): C 49.3 / 49.0, H 3.4 / 3.4, P 7.0 / 7.2, Ag 12.1 / 12.22

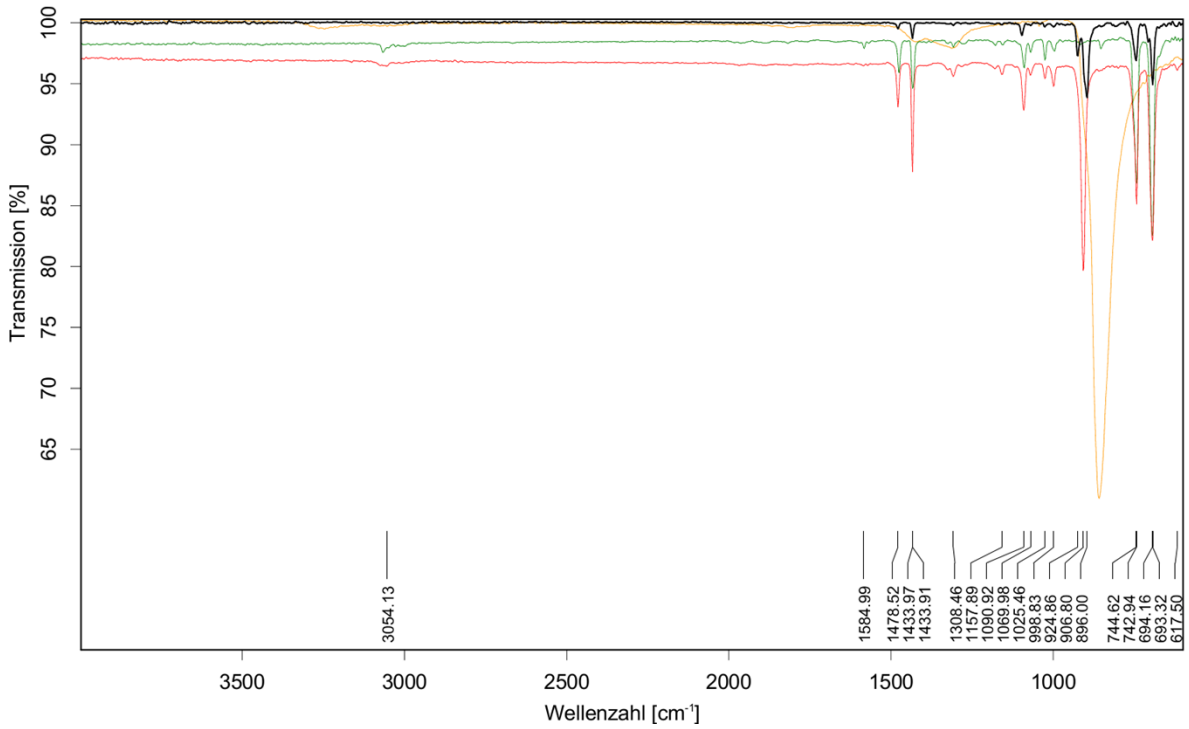

Fig. S2: IR spectra of $[(Ph_3P)_2AgReO_4]_2$ (black), PPh_3 (green), $AgReO_4$ (yellow), and $[Ag(PPh_3)_4][ReO_4]$ (red).

Table S1. Selected crystallographic data for the compounds.

Data	$[Ag(PPh_3)_4[ReO_4]$	$[(Ph_3P)_2AgReO_4]_2$
Sum formula	$AgC_{72}H_{60}O_4P_4Re$	$Ag_2C_{72}H_{60}O_8P_4Re_2$
Color	colorless	colorless
Habitus	block	block
Formula mass [g/mol]	1407.15	1765.22
Crystal System	trigonal	Triclinic
Space group (No.)	*R*3 (No.146)	*P*-1 (No. 2)
a [Å]	14.2192(1)	12.1764(4)
b [Å]	14.2192(1)	12.4966(3)
c [Å]	51.1145(9)	13.2647(5)
α [°]	90	89.938(2)
β [°]	90	62.745(3)
γ [°]	120	68.528(2)

[Å^3]	8950.0(2)		1635.6(1)
Z	6		1
$\varrho_{calc.}$ [g/cm^3]	1.56		1.79
λ [Å] ($Mo_{K\alpha}$)		0.71073	
T [K]		123(2)	
R_{int}	0.064		0.062
h	-23 to 24		-21 to 21
k	-25 to 25		-12 to 22
l	-89 to 90		-23 to 23
S ($I \geq 2\sigma(I)$, all data)	0.92, 0.92		0.78, 0.78
$R(F)$ ($I \geq 2\sigma(I)$, all data)	0.051, 0.095		0.040, 0.112
$wR(F^2)$ ($I \geq 2\sigma(I)$, all data)	0.128, 0.141		0.085, 0.075
Reflections/Parameters/Restraints	22832/496/1		18415/416/0
$\Delta\varrho_{max.}$ [eÅ^{-3}]; $\Delta\varrho_{min.}$ [eÅ^{-3}]	4.27, -3.42		3.16, -3.32

Both structures were solved using the Patterson method implemented in Shelxs and refined using Shelxle. $[Ag(PPh_3)_4][ReO_4]$ was refined as an inversion twin in spacegroup *R*3 in which one of the perrhenate anions is disordered. Refinements in the centrosymmetric space group *R*-3 showed a completely disordered ReO_4^- anion, worse R-values and the refinement did not converge. The residual electron density is located close to the Re atoms. The structure of the cyclic dimer only showed some disorder in the O-atoms not coordinating to Ag cations. All H-atoms were located and refined using a riding model. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), http://www.fiz−karlsruhe.de/icsd.html, on quoting the depository numbers CSD- 429166 for $[Ag(PPh_3)_4][ReO_4]$ and CSD- 429165 for $[(Ph_3P)_2AgReO_4]_2$.

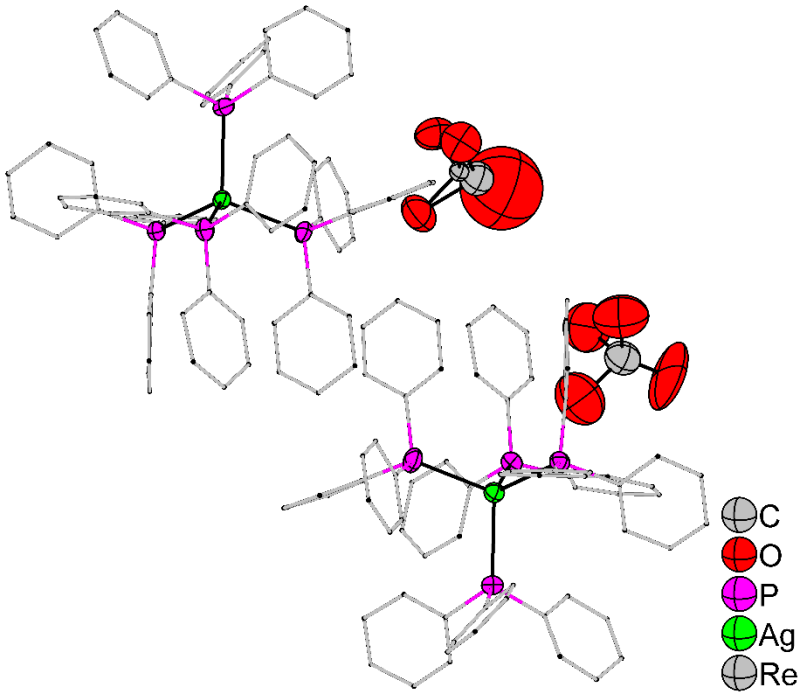

Figure S3. A section of the crystal structure of $[Ag(PPh_3)_4][ReO_4]$ where the disorder of one ReO_4^- anions becomes obvious. Thermal displacement parameters are shown at the 70 % level at 123 K. H atoms are omitted and the C atoms are shown as a wire-frame for the sake of clarity.