Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

A "one pot" mass spectrometry technique for characterizing solution- and gas-phase photochemical reactions by electrospray mass spectrometry

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Section S1: On-line photolysis apparatus

Section S2: Additional experimental details

Section S3: Isotope patterns

Section S2: TDDFT calculations of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2CO]^+$

Section S1: On-line photolysis apparatus

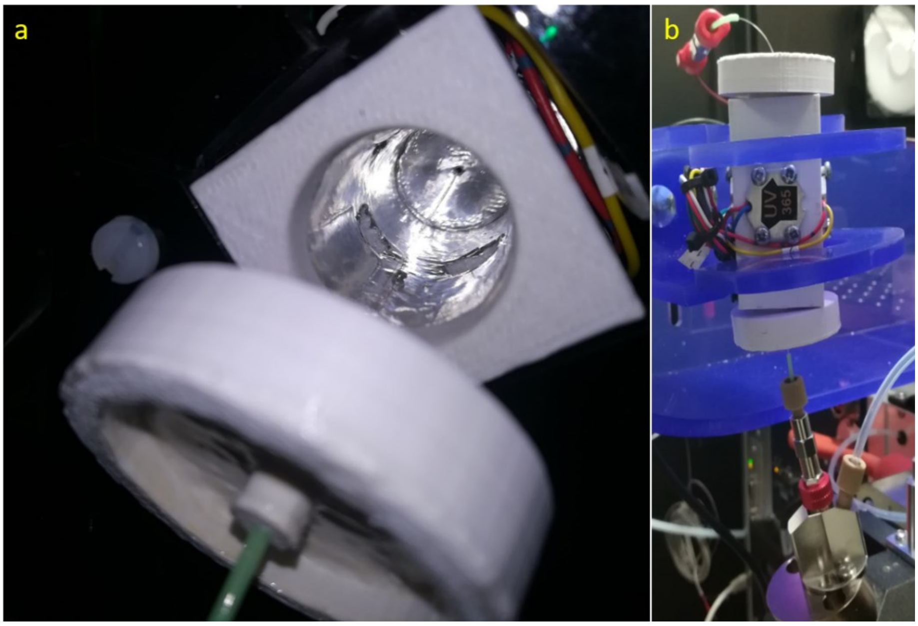


Figure S1: a) Pictures of the inside of the photolysis cell and b) photolysis cell mounted on top of the electrospray needle, in the experimental configuration.

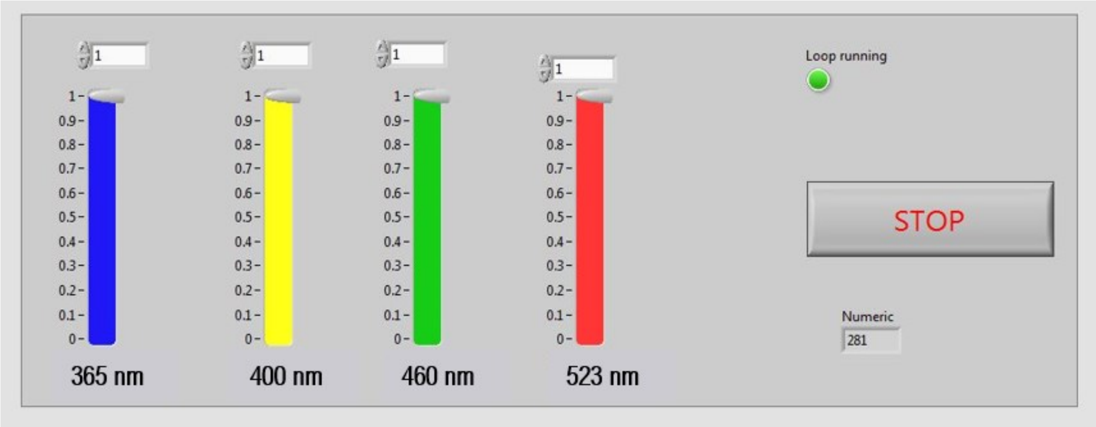


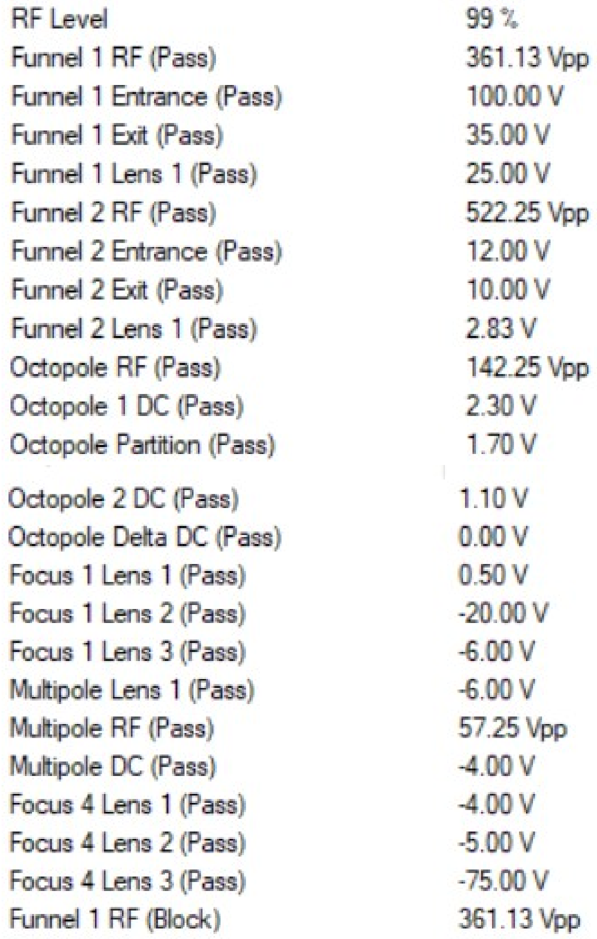
Figure S2: Interface of the LabVIEW software employed with the photolysis cell.

Section S2: Additional experimental details

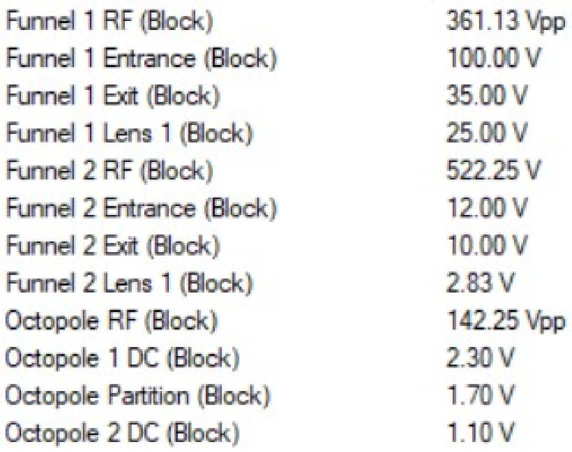
The ESI voltages used in the experiments conducted were as follows:

Capillary exit block: -200 V: Capillary exit: 140 V: HV Capillary: -3000 V: HV endplate offset: -500 V

Ion guide:



RF Level	99 %
Funnel 1 RF (Pass)	361.13 Vpp
Funnel 1 Entrance (Pass)	100.00 V
Funnel 1 Exit (Pass)	35.00 V
Funnel 1 Lens 1 (Pass)	25.00 V
Funnel 2 RF (Pass)	522.25 Vpp
Funnel 2 Entrance (Pass)	12.00 V
Funnel 2 Exit (Pass)	10.00 V
Funnel 2 Lens 1 (Pass)	2.83 V
Octopole RF (Pass)	142.25 Vpp
Octopole 1 DC (Pass)	2.30 V
Octopole Partition (Pass)	1.70 V
Octopole 2 DC (Pass)	1.10 V
Octopole Delta DC (Pass)	0.00 V
Focus 1 Lens 1 (Pass)	0.50 V
Focus 1 Lens 2 (Pass)	-20.00 V
Focus 1 Lens 3 (Pass)	-6.00 V
Multipole Lens 1 (Pass)	-6.00 V
Multipole RF (Pass)	57.25 Vpp
Multipole DC (Pass)	-4.00 V
Focus 4 Lens 1 (Pass)	-4.00 V
Focus 4 Lens 2 (Pass)	-5.00 V
Focus 4 Lens 3 (Pass)	-75.00 V
Funnel 1 RF (Block)	361.13 Vpp



Funnel 1 RF (Block)	361.13 Vpp
Funnel 1 Entrance (Block)	100.00 V
Funnel 1 Exit (Block)	35.00 V
Funnel 1 Lens 1 (Block)	25.00 V
Funnel 2 RF (Block)	522.25 V
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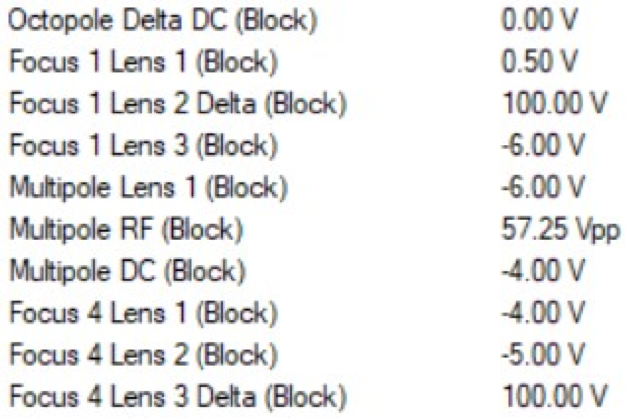
Octopole 1 DC (Block)	2.30 V
Octopole Partition (Block)	1.70 V
Octopole 2 DC (Block)	1.10 V



Octopole Delta DC (Block)	0.00 V
Focus 1 Lens 1 (Block)	0.50 V
Focus 1 Lens 2 Delta (Block)	100.00 V
Focus 1 Lens 3 (Block)	-6.00 V
Multipole Lens 1 (Block)	-6.00 V
Multipole RF (Block)	57.25 Vpp
Multipole DC (Block)	-4.00 V
Focus 4 Lens 1 (Block)	-4.00 V
Focus 4 Lens 2 (Block)	-5.00 V
Focus 4 Lens 3 Delta (Block)	100.00 V

Section S3: Isotope patterns

Figure S2 displays the experimental and simulated isotope pattern for **(**[Ru(η^5-C_5H_5)$(PPh_3)_2CO]^+$). The simulation confirms the assigned identity of the complex ion.

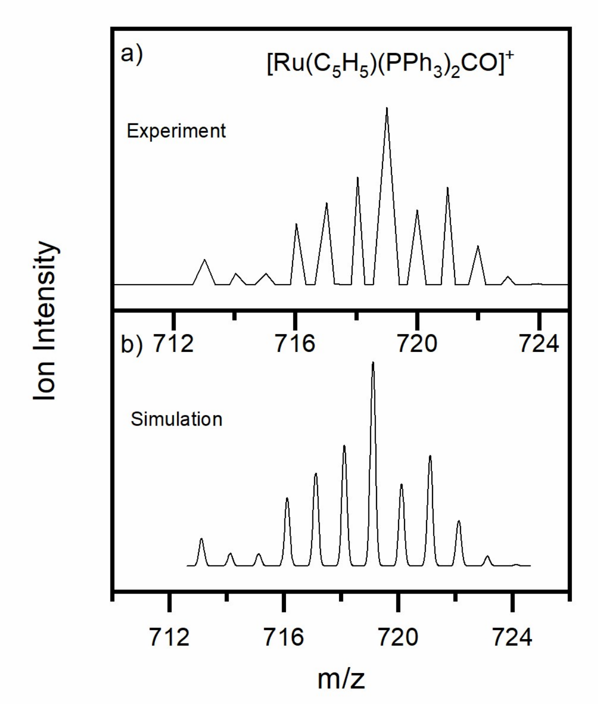
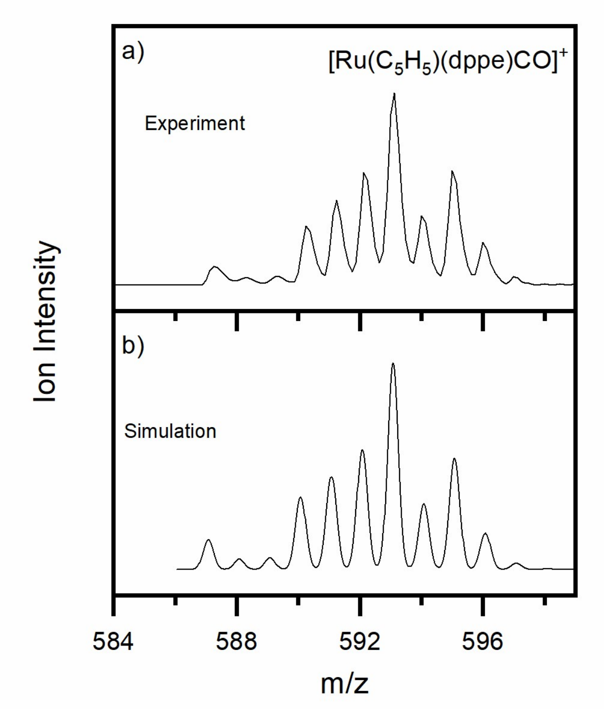


Figure S3 displays the experimental and simulated isotope pattern for **(**[Ru(η^5-C_5H_5)(dppe)$CO]^+$). The simulation confirms the assigned identity of the complex ion.



Section S2: TDDFT calculations of [Ru(η^5-C_5H_5)(PPh_3)$_2$CO]$^+$

TDDFT calculations were performed for compound **1 (**[Ru(η^5-C_5H_5)(PPh_3)$_2$CO]$^+$**)** at a number of different levels of theory. Prior to performing the TDDFT calculations, compound **1** was fully optimised at the PBE0/Def2-SV level, with ECP on Ru, with the global minimum structure being displayed in Fig. S3.

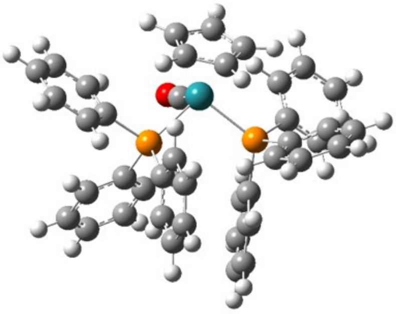


Figure S3: Global minimum structure of compound1 at the PBE0/Def2-SV level with ECP on Ru.

The calculated absorption spectra obtained from the TDDFT calculations are shown in Fig. S4. The B3LYP/6-31G* with SDD on Ru calculated spectrum is closest to the experimental photodepletion spectrum. Table S1 reports a comparison between the experimental and computational excitation energies, and Table S2 lists the main transitions between 3 and 4.7 eV. The orbitals that are involved in these transitions are shown in Fig. S5. The orbital character in these transitions are all a combination of the metal d orbitals and the ligand π orbitals. In all of the density functional calculations studied here, numerous highly-mixed transitions are predicted at energies higher than 4.7 eV.

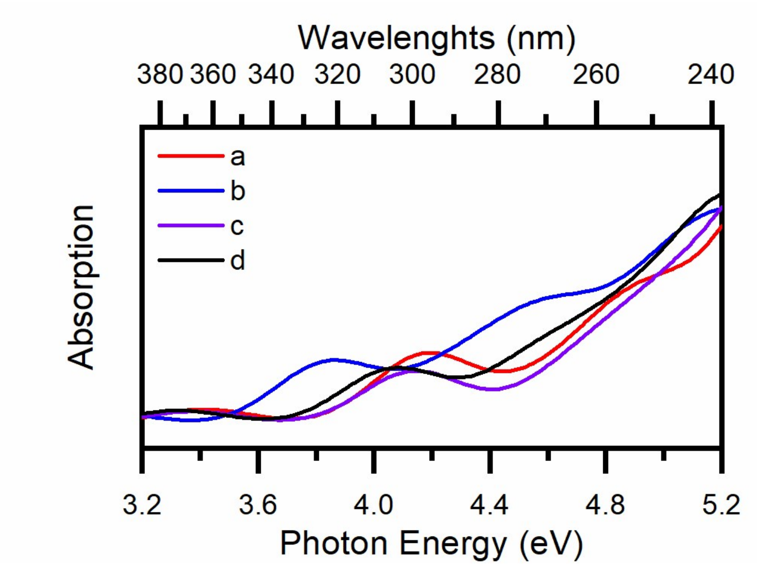


Figure S4: Calculated absorption spectra of complex 1 at a) PBE0/6-31G*, b) B3LYP/6-31G*, c) PBE0/Def2-SV and d) B3LYP/Def2-SV theory levels. ECP core potential of Ru is always included.

Table S1: Comparison between experimental absorption maxima and calculated absorption maxima at different levels of theory. The energies are given in eV.

Experimental	**PBE0 6-31G***	**B3LYP 6-31G***	**PBE0 Def2-SV**	**B3LYP Def2-SV**
-	3.4	3.1	3.4	3.3
3.9	4.2	3.8	4.1	4.1
4.6	4.8	4.6	4.8	4.8
5.1	5.4	5.2	5.4	5.2

Table S2: Calculated TDDFT transition energies and oscillator strengths of complex 1. Calculations were performed at the B3LYP/6-31G*/SDD level. Only transitions below 4.7 eV, and with oscillator strength > 0.01 are listed.

Orbital transitions	**Photon energy**/eV	**f**
(0.87)170→171	3.06	0.0151
(0.72)170→172	3.75	0.0147
(0.48)169→171 (0.10)170→172	3.85	0.0615
(0.54)169→172	4.17	0.0267
(0.52)168→172	4.31	0.0274
(0.25)167→171 (0.16)156→172	4.37	0.0199
(0.34)166→171 (0.17)168→171	4.51	0.0204
(0.23)166→171	4.57	0.0264
(0.65)170→173	4.60	0.0225
(0.58)162→171	4.67	0.0124
(0.29)170→174	4.67	0.142

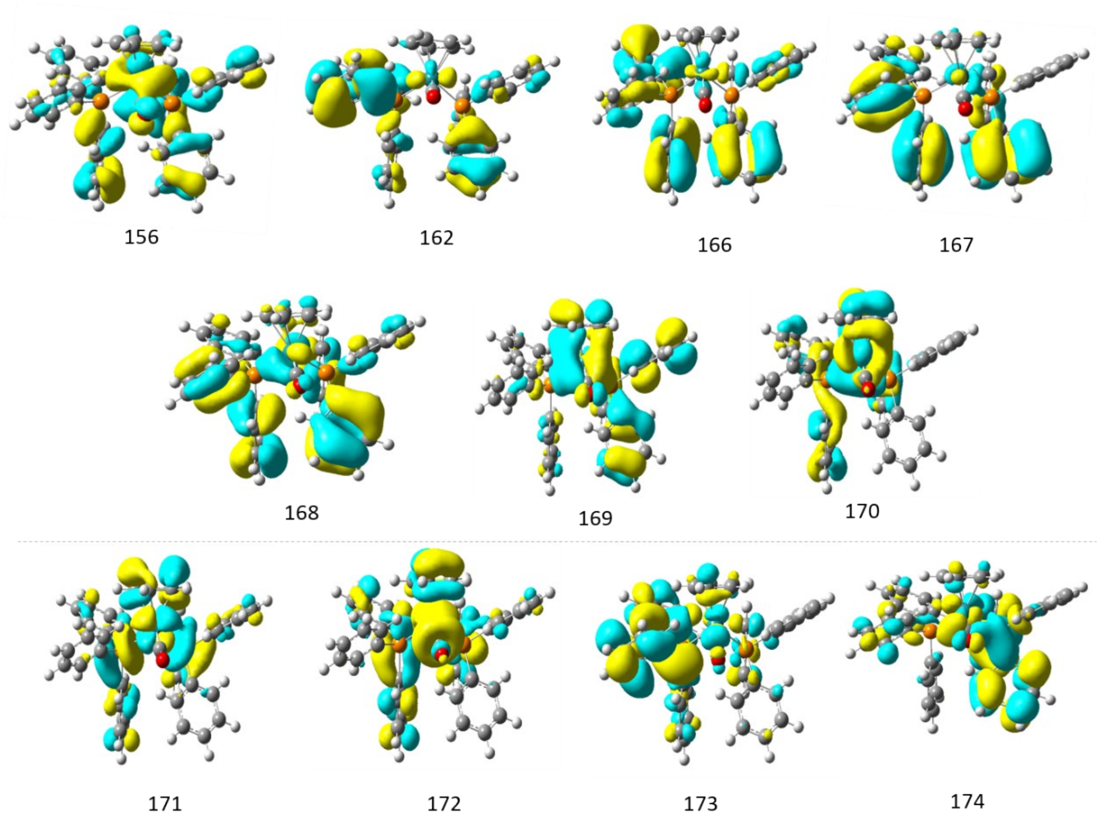


Figure S5: **Molecular orbitals of 1 involved in the transitions predicted by TDDFT calculations between 3.06 – 4.67 eV described in Table S2. The iso-value for each orbital surface is 0.02 e/au^3. The dashed line indicates the se**paration between occupied and unoccupied orbitals.